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ENVIRONMENTAL HEALTH SERIES
Radiological Health

RADIOASSAY PROCEDURES FOR ENVIRONMENTAL SAMPLES

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

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RADIOASSAY PROCEDURES FOR ENVIRONMENTAL SAMPLES

January 1967

National Center for Radiological Health

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ABSTRACT

This is a manual of methods used in laboratories of the Public Health Service's National Center for Radiological Health of the Bureau of Disease Prevention and Environmental Control for the determination and interpretation of the radionuclide content of samples collected for environmental surveillance.

Step by step procedures are given for the analysis of milk, food, air, water, and other environmental samples. A discussion of instrumentation for these procedures is given, and a program of analytical quality control is described.

Appendices include a definition of laboratory practice and terminology and instructions for preparing required reagents. Bibliographic references are included for specific procedures as well as for more general discussions.

The use in this manual of trade names of commercially available products does not constitute an endorsement of the product by the Public Health Service and does not imply that there are no other suitable products available.

FOREWORD

Environmental radiological surveillance is a major responsibility of the National Center for Radiological Health, Bureau of Disease Prevention and Environmental Control, Public Health Service. Until 1967 the National Center was the Division of Radiological Health, Bureau of State Services, Public Health Service.

Radiological surveillance activities of the Public Health Service began in 1951. In August 1959 the President assigned to the Department of Health, Education, and Welfare the primary responsibility for collation, analysis, and interpretation of data on environmental radiation levels. This responsibility emphasized the need for reliable and uniform analytical procedures.

The surveillance laboratories develop assay procedures that are used routinely and are published by each laboratory in a manual intended primarily for its own use. The present manual is the first compilation of procedures used by the individual laboratories.

The National Center invites comments and suggestions from readers of this manual with respect to any of its Sections. Questions on specific problems related to radioassay procedures should be addressed to the National Center for Radiological Health. These will be referred to the appropriate laboratory staff member who will be pleased to furnish information or consultation.

James G Terrill

James G. Terrill, Jr., Director,
National Center for Radiological Health

January 1967

PREFACE

The analytical procedures used in the collection and evaluation of radiological health data were developed at the laboratories of the National Center for Radiological Health.[1] This manual is a compilation of procedures developed by these laboratories and used to obtain data published by the National Center. These data are published in Radiological Health Data and Reports, the monthly publication of the Center since April 1960.

The analytical procedures outlined in this manual have been used in the analyses of thousands of routine and special environmental samples. They have been checked through an intra- and interlaboratory analytical quality control system. The procedures are intended for application to relatively large numbers of samples in programs involving continuous surveillance. Some procedures may no longer be in use by the time of publication, but this does not invalidate them. Replacement procedures are not necessarily improvements, but may be more convenient or more suited to the equipment of a particular laboratory or to new facilities. For certain purposes, especially research investigations, more precise methods than those presented in this manual may be required.

Scientific staff members of the National Center for Radiological Health principally responsible for contributing the procedures appearing in this manual are: Edmond J. Baratta, Esther S. Ferri, Abraham S. Goldin, Gerald J. Karches, Harry E. Kolde, Georgia I. Lindsey, Charles R. Porter, Marvin Rosenstein, John L. Russell, Lloyd R. Setter, and Ann B. Strong. Without their active participation and cooperation over the extended period required for a compilation of this magnitude, the manual could not have been produced.

Geneva S. Douglas
Editor

Las Vegas, Nevada
January 1967

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[1] Northeastern Radiological Health Laboratory, Winchester, Massachusetts; Nuclear Engineering Laboratory, Cincinnati, Ohio; Radiological Health Laboratory, Rockville, Maryland; Southeastern Radiological Health Laboratory, Montgomery, Alabama; and Southwestern Radiological Health Laboratory, Las Vegas, Nevada.

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SECTION 0

INTRODUCTION

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SECTION 0. INTRODUCTION

The program objective of the National Center for Radiological Health* is the prevention and control of radiological hazards to the public from X rays, tests of nuclear devices for military and peaceful applications, experimental nuclear reactors, industrial and medical uses of isotopes, and other sources of radiation exposure. In pursuing its objective, the Center conducts and supports basic and applied research, provides technical assistance to the States, assists in training radiological health specialists, and engages in environmental surveillance programs for collecting and assessing data on all forms of public radiation exposure throughout the Nation.(1)

The Center's research activities include investigations coordinated with and in support of its environmental surveillance programs. Bionomic studies are in progress to better define the transport of the more important radioactive contaminants from their source to their ultimate deposition in man. Coordinated studies at the Center's laboratories are associated with atmospheric contamination encountered under small controlled releases or under accidental release conditions from nuclear installations and the nuclear testing program of the United States and foreign countries. Other investigations have been directed toward understanding the relationship between stable and radioactive elements in the diets of animals. These bionomic studies are aimed at determining the critical points in the transport pathway at which to collect samples to provide data which will enable rapid and precise predictions of the ultimate dose to man and the points at which to induce alterations in the transport chain as effective and feasible preventive measures.

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* Effective January 1, 1967 the Division of Radiological Health, established in July 1958, became the National Center for Radiological Health in the new Bureau of Disease Prevention and Environmental Control.

The Center's environmental surveillance programs maintain and operate nationwide sampling networks and special networks for monitoring and sampling the environment in public areas surrounding U. S. nuclear test sites and experimental nuclear reactor sites. Information from these networks has two primary applications. The first of these is to provide data for estimating public exposure and doses relatable to environmental radioactivity. The second is to provide a system responsive to changes in radioactivity levels in the environment so that the changes may be explored in more detail as to origin and the possible need for corrective action.

These surveillance activities include the collection and analysis of samples of air, water, milk, total diets, bovine thyroid glands, human and animal bones, and special samples relating to human body burdens and doses. Analysis of the network samples is performed at the Center's radiological health laboratories under rigid interlaboratory quality control. The data are reported regularly in the technical monthly, *Radiological Health Data and Reports*, published by the National Center for Radiological Health as a permanent record on sources and levels of environmental radioactivity.

0.1 USE OF THE MANUAL

The methodology presented here has been used routinely and successfully by the Center's laboratories to determine radionuclide and related stable element concentrations in a large number of samples. The methods are designed to assure accuracy and comparability of results and should be most useful to Federal, State, local, and university laboratories with radiological health analytical capabilities. Their compilation will also serve as a detailed reference on analytical procedures through which the Center's published data are or have been derived.

The methods are not standard methods, but were developed or adapted to meet the program requirements of the Center's laboratories, each of which seeks new ways to improve the methodology for measuring radioactive contaminants in the environment. As the need arises for routine measurement of additional nuclides, efforts are made to improve sampling and analysis sensitivity for such radionuclides as carbon 14, tritium, and radioactive isotopes of noble gases, and ways to adapt research methods for analyzing large numbers of samples are sought. When thoroughly tested, such modifications are incorporated into the continuing analyses of radioiodines, radiostrontium, barium 140, cesium 137, and other currently routine analyses.

Most of the methods are presented as step by step "cookbook" procedures. Nevertheless, many users of this manual will not have the expert personnel and highly specialized and complex equipment needed for certain of the techniques presented. The user should select methods suitable to his facilities and to his surveillance program needs. Assistance from laboratories of the National Center for Radiological Health is available to States having specific need for highly specialized analytical work. In addition, technical assistance and field consultation is available to the States as on-the-job laboratory training.

Analytical methodology for radiological health surveillance programs is not static. The arrangement of contents, pagination, and numbering of subdivisions in this document were chosen in recognition of the impossibility of publishing a compilation of methods in current use by the Center's laboratories, and the consequent need for continual updating. As modifications of current procedures and new or improved methods, techniques, and apparatus are developed and put into practice, they will be published as supplements or addenda.

0.2 LABORATORY SAFETY

Laboratory safety concerns not only the safety of workers and efficient operation of the laboratory, but the health and safety of people living and working near the laboratory as well. It is of utmost importance, therefore, that laboratory safety be a major consideration in design and operation of the analytical laboratory.

Any analytical laboratory should establish for itself a comprehensive safety plan or protocol to fit its own procedures, personnel, and physical facilities. Administrative responsibility for laboratory safety lies with supervisory staff and ultimately with the director of the laboratory. However, a well-planned safety program is successful only to the extent that all laboratory personnel assume their individual responsibilities in following the prescribed plan. Laboratory workers should be well instructed not only in the analytical procedures being performed, but also in the safety measures associated with them.

Analyses in this manual require no unusual safety measures. Although the procedures are for radioassay, the samples themselves constitute no hazard greater than that of the environment from which they were taken. The most likely source of potential radiation hazard is the undiluted radioactive solution obtained for purposes of preparing spiked samples for tracer studies or standards for calibration, performance references, or quality control.

People who are to work with radioactive materials or radiation-producing machines should be thoroughly trained in their proper use. Basic radiological safety regulations appropriate to the license held by the laboratory for use of such materials and machines are set forth by the Atomic Energy Commission in the *Code of Federal Regulations, Title 10 — Atomic Energy*(2). Rules and guides for general, chemical, biological, and radiological safety in laboratories are well-documented and readily available in published literature.(3,4,5,6,7) By referring to such literature and following the radiological safety regulations appropriate to the license held by the laboratory, a satisfactory safety protocol can be developed.

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SECTION 1.

INSTRUMENTATION

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SECTION 1. INSTRUMENTATION

1.0 INTRODUCTION

Radioactivity in samples is measured by counting either alpha, beta, or gamma emissions. Each form of energy release requires a different technique to measure it efficiently. The purpose of the instrumentation section is to assist the analyst in selecting the proper instrument and interpreting his data, and to provide him with information on calibrating his instruments and maintaining a well-run counting room.

The methods for detecting radiations vary, but the basic concept is to capture part or all of the energy released through decay, and to convert it into a current flow or pulse which can be recorded. Laboratories of the National Center for Radiological Health use a variety of sensitive instruments which are the pulse recording type. The gross count can be taken by totaling the pulses recorded on scalers. For spectral analysis, the pulses are sorted out by energy, and the number of pulses counted in each energy band is stored separately. A pulse height analyser is used for this spectral analysis.

Most environmental surveillance samples have low activity. Therefore, background radiation seen by the detector, such as natural activity in the earth and cosmic rays, must be minimized. Massive shielding and special electronic circuitry are used for this purpose.

Some of the important considerations in the selection of the proper instrument are:

1) the type of radiation emitted - alpha, beta, gamma
2) the energy of the emission
3) the condition of the sample when prepared for counting

4) the activity level of the sample
5) the radionuclide composition of the sample
6) the accuracy needed or desired

The preparation of samples and standards for calibration of the selected instrument also depends upon these points as well as on the type of data needed. Qualitative data identify the radionuclides present, whereas quantitative data determine how much of each is present. Spectrometry can provide both types of data depending on the extent to which the spectrum is analyzed. Without spectrometry, radiochemistry quantitatively isolates the element (a qualitative separation of the nuclide) so that the quantity of radionuclide present can be counted.

When the analyst has determined the type of instrumentation he needs, or at least has carefully identified his counting requirements, he can contact instrument manufacturers selected from a list published annually in the *Nucleonics - International Buyers Guide*(1). A reliable manufacturer can usually provide additional information as to the best equipment for a particular application from his list of instruments.

1.1 INSTRUMENTS FOR MEASURING RADIOACTIVITY

Instruments for measuring radioactivity make use of the ionizing properties of nuclear radiation. Basically they provide a medium with which the radiation can interact and a means of detecting and identifying this interaction. All instruments can be classified by their interaction medium under three general categories: gas ionization detectors, scintillation detectors or phosphors, and solid state detectors. Instruments used by the National Center for Radiological Health to measure radioactivity of environmental samples fall into the first two categories.

When a charged particle such as an alpha or beta particle moves through a gas at high velocity it may act on a gas molecule or atom to remove an electron and produce an ion pair. Gas ionization detectors contain an enclosed volume of gas in which two collecting electrodes are placed. When a direct voltage is applied across these electrodes in the presence of ionizing radiation, five types of response will be observed as the voltage is increased. By plotting the number of ion pairs collected against applied voltage one obtains a curve such as that in Figure 1.1-1 showing five distinct regions of response.

In the ion recombination region many of the ion pairs recombine with each other before reaching the collecting electrode. Gas ionization instruments are not operated in this region of response.

In the ionization chamber region the applied voltage is sufficient to prevent significant recombination of ion pairs and the ions are collected in a one-to-one ratio with those formed. Ionization chamber instruments operate in this region of response.

At voltages in the proportional region the ions are accelerated to achieve enough energy to produce secondary ionization in the gas medium, thus amplifying the primary ion current. Although the ion current or pulse size is amplified, to an extent described by the "gas amplification factor", it is still proportional to the energy of the incident particle or radiation. Thus gas ionization detectors operating in the proportional region can detect alpha particles selectively in the presence of beta (or gamma) radiation. Alpha and beta proportional counters with or without windows to separate samples from the gas ionization medium operate at voltages in the proportional region of response.

Geiger counters, or GM counters, operate in the Geiger-Mueller region where the gas amplification factor is so large that an avalanche of electrons spreads along the entire length of the anode. Here the pulse size is independent of the number of primary ions or energy of the incident radiation. This accounts for the high sensitivity of GM detectors and their inability to distinguish between the various types of radiation.

In the continuous discharge region the gas amplification factor is so large that the gas begins to arc generating a series of self-perpetuating discharges. Operation of any gas ionization instrument at voltages in this region even for a few seconds will seriously damage the electrodes.

Scintillation detectors make use of the long-known ability of ionizing radiations to produce short-lived flashes of light (scintillations) in phosphors. The light flashes can produce photoelectrons from a photosensitive cathode in a photomultiplier tube and these photoelectrons are further amplified into a pulse which can be counted. When the scintillator is large enough to absorb all the energy of the radiation in the excitation and ionization interaction, the output pulse will be proportional to the energy of the incident radiation. This proportional response is necessary for gamma scintillation spectrometry. Scintillators are of many materials including organic crystals such as anthracene, liquid solutions of an organic scintillator such as *p*-terphenyl in an organic solvent, solid solutions of an organic scintillator in a plastic solvent (plastic scintillation detectors), inorganic crystals such as sodium iodide or zinc sulfide, and noble gases. Only a few of the many types of scintillation detectors are used by National Center for Radiological Health laboratories to count radioactivity in environmental samples.

Solid state detectors make use of the property of some insulators such as diamond or silver chloride crystals, or semiconductors such as germanium or silicon, to show an instantaneous conductivity when high-energy particles or radiation interact with the material of which they are composed. These detectors have been used experimentally and for special counting applications which are not within the scope of this manual.

This Section briefly describes the application and operation of counting instrumentation used by Division of Radiological Health laboratories in conjunction with the radiochemical procedures presented in other Sections of the manual. A more extensive treatment of the subject is being prepared by the Center's Interlaboratory Technical Advisory Committee. This document(2) will be of particular value to the novice in radioactivity measurement and to those who must select and purchase instrumentation for the determination of low levels of radioactivity in environmental samples.

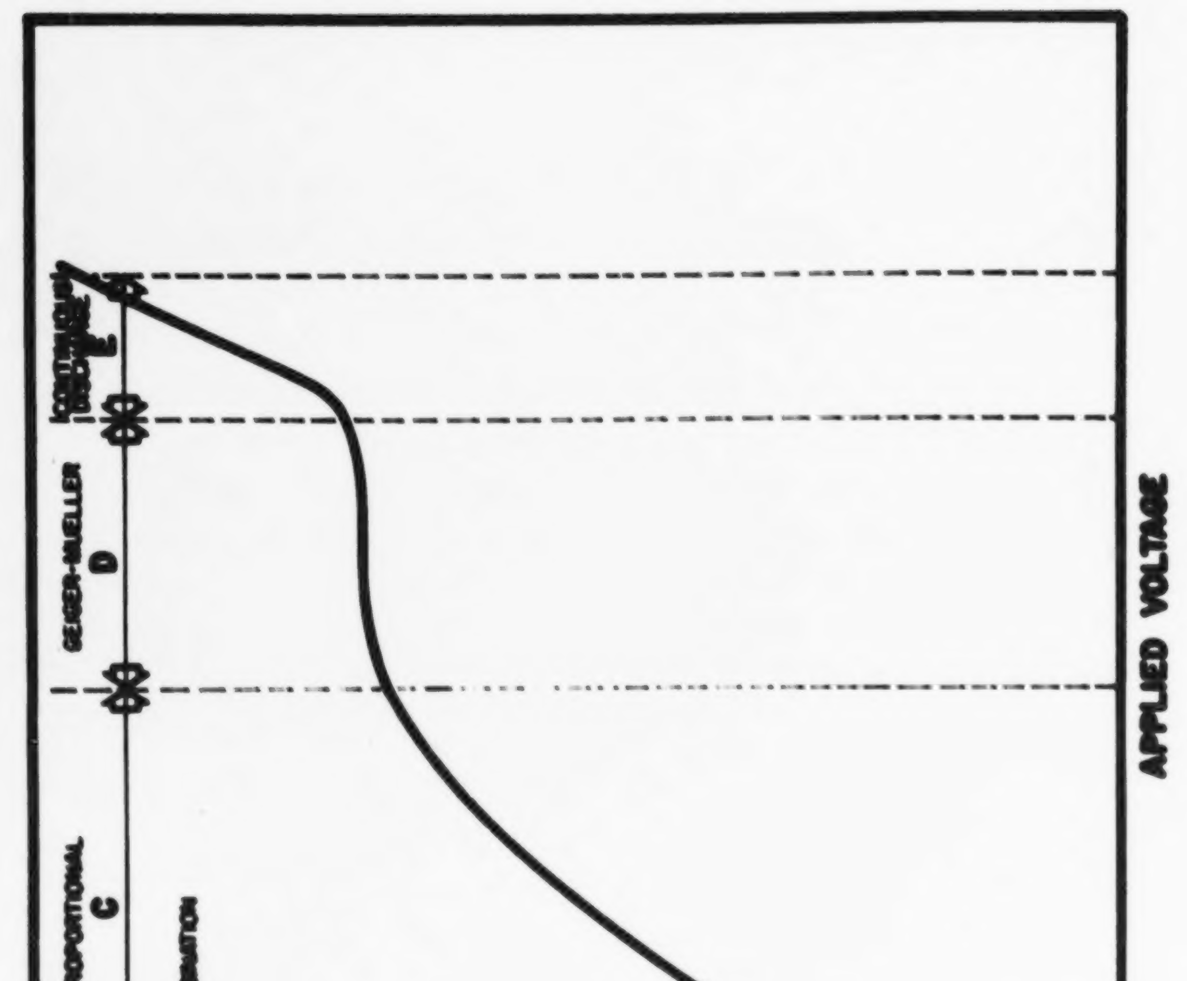


Figure 1.1-1 Regions of instrument response

1.1.1 Alpha Activity

Alpha particles are helium nuclei and carry a positive charge equal to twice the electron (beta) charge. Alpha particles, like gamma rays, are monoenergetic emissions. The most commonly counted alpha emitters, such as radon and thoron daughters, have energies of 5 to 7 million electron volts (Mev) and a mean range in air of about 5 centimeters. Samples to be counted for these particles should be very thin to minimize loss of energy in the sample through self-absorption, and should have little or no distance between the sample and the detector to minimize loss of energy in air. Because of the low penetrating power of alpha particles, end-window counters are generally unsatisfactory for alpha counting unless the window thickness is 0.1 milligram per square centimeter or less.

For each instrument described, there is an operating high voltage which will yield consistent counting results. To determine the operating voltage, counts are made with a known alpha source at 50-volt increments. The initial counts will appear at the threshold voltage of the instrument, the lowest voltage at which pulses are detected. As the voltage is increased, more counts are observed, until a leveling-off of the count rate occurs. This level area, or plateau, continues until there is a sharp increase in the counts. The operating voltage is selected midway along the plateau. The manual provided with each commercially available instrument usually discusses in some detail the selection of the probable operating voltage.

After the operating voltage has been selected, calibration must be performed to obtain quantitative data. Calibration involves selecting a suitable standard, preparing it in a form to simulate the samples, and counting the calibration standard at the selected operating voltage. Refer to 1.3 RADIOACTIVE STANDARDS for a complete discussion of calibration standards. For calibrating alpha counters, sample thickness must be considered because self-absorption in the sample can be severe.

Performance standards are a very necessary part of routine counting. Their use insures that the counter is functioning the same when the sample is counted as it was when calibration was performed. Preparation and use of performance standards are discussed in 1.4.1 Performance Standards.

Background count rate should be determined at least twice daily to detect possible fluctuations caused by contamination, radio-frequency or line-current pulses, or by a change in the natural background radiation from radon-thoron daughters in the air or from cosmic radiation. A change in background due to contamination of the counter is most apt to occur if the samples are placed within the detector for counting.

INTERNAL PROPORTIONAL ALPHA COUNTER

Application

Internal proportional alpha counters are gas-flow counters useful for measuring levels of alpha activity commonly found in environmental samples. The counters are termed "internal" because the sample is placed into the sensitive part of the detector, and counting gas is purged throughout both counting chamber and sample. Because of this procedure, the counter can be contaminated by the sample. At the same time, this essentially eliminates all losses but those from self-absorption. For samples deposited on a planchet, this counter is as sensitive as any alpha counting system, and can be used to count activities ranging from the lowest to the very highest.

To be detected, the alpha particles have only to penetrate the sample itself and produce several ion pairs in the gas. The detector is almost equally sensitive over the inside diameter, although a slight decrease in response is noted at the edge of the counting dish. Any metallic planchet is suitable for counting in an internal proportional counter, but care should be taken to have the solids uniformly distributed in the dish. This is especially true for counting alpha activity if there is much solid material in the sample, as absorption losses from unevenly distributed solids will be inconsistent. Stainless steel dishes are used for most samples, but for plating some radionuclides, silver or nickel disks are used. This is illustrated by the method for polonium 210 in 7.2.4 of SECTION 7. OTHER ENVIRONMENTAL SAMPLES.

Operation

The counters are termed "proportional" because they operate at voltages where the size of the pulse is proportional to the number of ion pairs produced. A counting gas mixture of 90 percent argon and 10 percent methane (P-10 gas) is commonly used. The electrons from ion pairs produced in this gas are collected by the central electrode to generate a pulse which is recorded by a scaler. Since alpha particles dissipate more energy in the chamber than beta particles, they produce more ion pairs and consequently larger pulses. The smaller beta-gamma pulses, if present, are discriminated against by operating at the relatively low voltage of approximately 1000 V which produces a small amplification. Ability to count only alpha emissions at one voltage and alpha plus beta-gamma emissions at another makes the proportional counter a versatile detector.

If the instrument used for counting samples of high activity is also used for counting those of low activity, background measurements should be more frequent than twice daily to check for contamination. For an unshielded 2¼-inch diameter hemisphere and piston, the alpha background is about 0.2 counts per minute.

The alpha counting efficiency for weightless samples is slightly higher than 50 percent. The efficiency for anything but weightless samples is substantially lower due to severe self-absorption losses.

The internal proportional counter is illustrated in Figure 1.1.1-1.

ALPHA SCINTILLATION COUNTER — Zinc Sulfide Screen

Application

The alpha scintillation counter is used for counting flaky or dusty samples such as air samples, that could easily contaminate an internal proportional counter. Uneven self-absorption losses from these samples can result in poor reproducibility, even with the scintillation counter. This instrument lends itself quite readily to mobile laboratory or field use because no gas supply is needed.

Since the sample is external to the detector, the counting dish or planchet need not be conducting. It should be shallow enough to enable the sample to be placed close to the zinc sulfide screen to minimize air absorption losses. In this configuration, the alpha scintillation counter is almost as sensitive as the internal proportional counter. Samples deposited on membrane filters provide a nearly ideal geometry because they are flat and usually evenly distributed. Self-absorption, however, can be severe for air samples having a high solids content.

Operation

The counter is composed of a zinc sulfide screen (zinc sulfide deposited on lucite or some other transparent substance), and a photomultiplier tube housed in a light-tight box coupled through a cathode follower into a scaler. The voltage that must be used depends on the photomultiplier tube characteristics. The tube should have a uniform photo-cathode which yields a satisfactory plateau. No additional amplification of the pulses is required, and operating voltages are usually less than 2000 V, enabling use of the simplest scalers.

A 2-inch diameter weightless sample close to a 3½-inch screen has a counting efficiency greater than 40 percent. For the same weightless sample, the efficiency will be about 50 percent in an internal proportional alpha counter. The efficiency obtained is much better than for an end window alpha counter, since the zinc sulfide screen has no window.

The background is about 0.2 cpm for a 3½-inch detector, and the plateau is about 200 volts long with a 2- to 3-percent slope per 100 volts. For additional information on operating and trouble shooting, the manufacturer's instrument manual should be consulted.

A typical alpha scintillation counter with zinc sulfide screen is illustrated in Figure 1.1.1-2. The radon counter, illustrated in Figure 1.1.1-3 is a specialized alpha scintillation detector in which the Kovar metal scintillation cell replaces the zinc sulfide screen.

ALPHA SCINTILLATION COUNTER — Liquid Scintillation

Application

The liquid scintillation counter was designed primarily for counting weak beta emitters such as tritium (^3H) and carbon 14. It can also be used successfully for alpha counting. Its chief advantage is that there can be no self-absorption losses in the sample to cause non-reproducible counting. Sample preparation may require some training in radiochemistry.

The samples are mixed with the scintillator and the mixture is placed in low potassium-content glass or polyethylene vials. The alpha counting efficiency approaches 100 percent, and the minimum sensitivity for radium 226 is about 0.2 picocurie per sample for a 100-minute count.

An alternate method is to place the sample in a small vial coated with zinc sulfide powder. With this procedure, the background is about 0.02 counts per minute, and the minimum sensitivity for radium 226 is approximately 0.02 picocurie per sample for 100-minute counting periods.

The liquid scintillation for alpha counting has not been used extensively by the Center's laboratories; but it is described here as an alternate to the more specialized radon emanation technique which follows.

Operation

A typical liquid scintillation counter uses two photomultiplier tubes in coincidence. Noise pulses originating in the tubes can be discriminated against as they are much smaller than alpha pulses. With the coincidence circuit, pulses must occur simultaneously in each tube to be recorded as a count.

The procedure for sample preparation involves radiochemical techniques which are beyond the scope of this Section of the manual. Instead, two references are given to enable those interested to obtain more detailed information. These are *Determination of Radium 226 in Food, Biological, and Environmental Samples* by J. A. Dapolito, *et al.*(3) and an article by H. I. Sax in Volume 32 of *Analytical Chemistry*(4).

RADON COUNTER — Gas Phase Counting

Application

The radon counter is used for the determination of radium 226 by measuring radon 222 and its daughters. The daughters of importance to the determination are the short-lived alpha emitters polonium 218, bismuth 214, and polonium 214. Lead 214 which follows polonium 218 in the decay chain is a beta emitter. Through sample preparation and handling techniques discussed in SECTIONS 4 and 5 of this manual, the radon gas is contained in a scintillation cell made of Kovar metal. This alpha scintillation cell is illustrated in Figures 4.2.4-3 and 1.1.1-3.

Gas phase scintillation counting yields the maximum sensitivity for radium 226. With appropriate sample preparation, it can be used for almost any sample for activities down to 0.01 picocurie per sample if 1,000-minute background and sample counts are made.

Operation

The radium 226 is stored in a sealed tube until the system has reached secular equilibrium (about 28 days) or at least until an amount of radon 222 sufficient for counting has grown into the radium 226 solution. Then the radon gas is purged into the evacuated scintillation cell by using radon-free gas, such as aged air or nitrogen, at a low purge rate. The cell containing the radon must be stored in a light-tight container for approximately 5 hours to enable the radon daughters to reach equilibrium. At equilibrium, for every radon 222 disintegration three alpha particles will be available for counting. This storage time can vary as long as the degree of equilibrium attained is considered in the calculation of radium 226 activity. The storage time should be long enough to allow any actinon (^{219}Rn) or thoron (^{222}Rn) daughters of radium 223 or radium 224, if present, to decay out. It is usually convenient to store the cell in the same light-tight container which houses the photomultiplier tube.

From its photomultiplier tube, which detects the light flashes in the cell, to its scaler, this counter is very similar to the zinc sulfide screen already described. The scintillation cell substitutes for the screen as the detector.

The counter is plateaued and calibrated by preparing a standard solution of radium 226 and processing the standard in the same manner as the samples are processed. This determines the efficiency of the purge and the counting.

Counting efficiency for the radon and daughters is approximately 80 percent in a properly coated cell. The background is usually 0.1 count per minute. Each cell must be checked independently on the phototube used for sample counting. It is important to keep the cell and the tube as a matched unit, as each can affect background and counting efficiency.

The typical radon counter is illustrated in Figure 1.1.1-3. Diagrams of the radon transfer apparatus, the radon bubbler or emanation tube, and the scintillation cell are shown in Figures 4.2.4-1 through 4.2.4-4 of SECTION 4. FOOD.

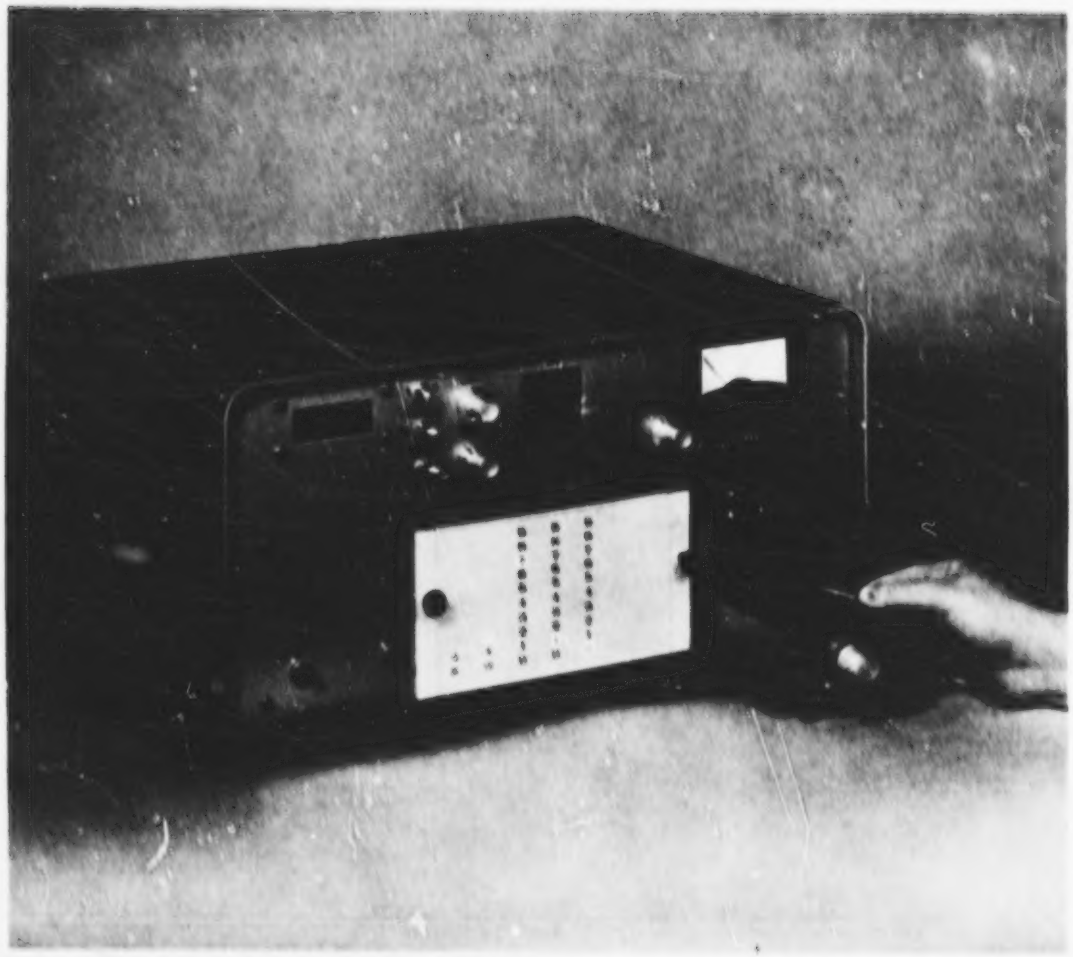


Figure 1.1.1-1 Internal proportional counter

Photograph courtesy of Nuclear Measurements Corporation, Indianapolis, Indiana.

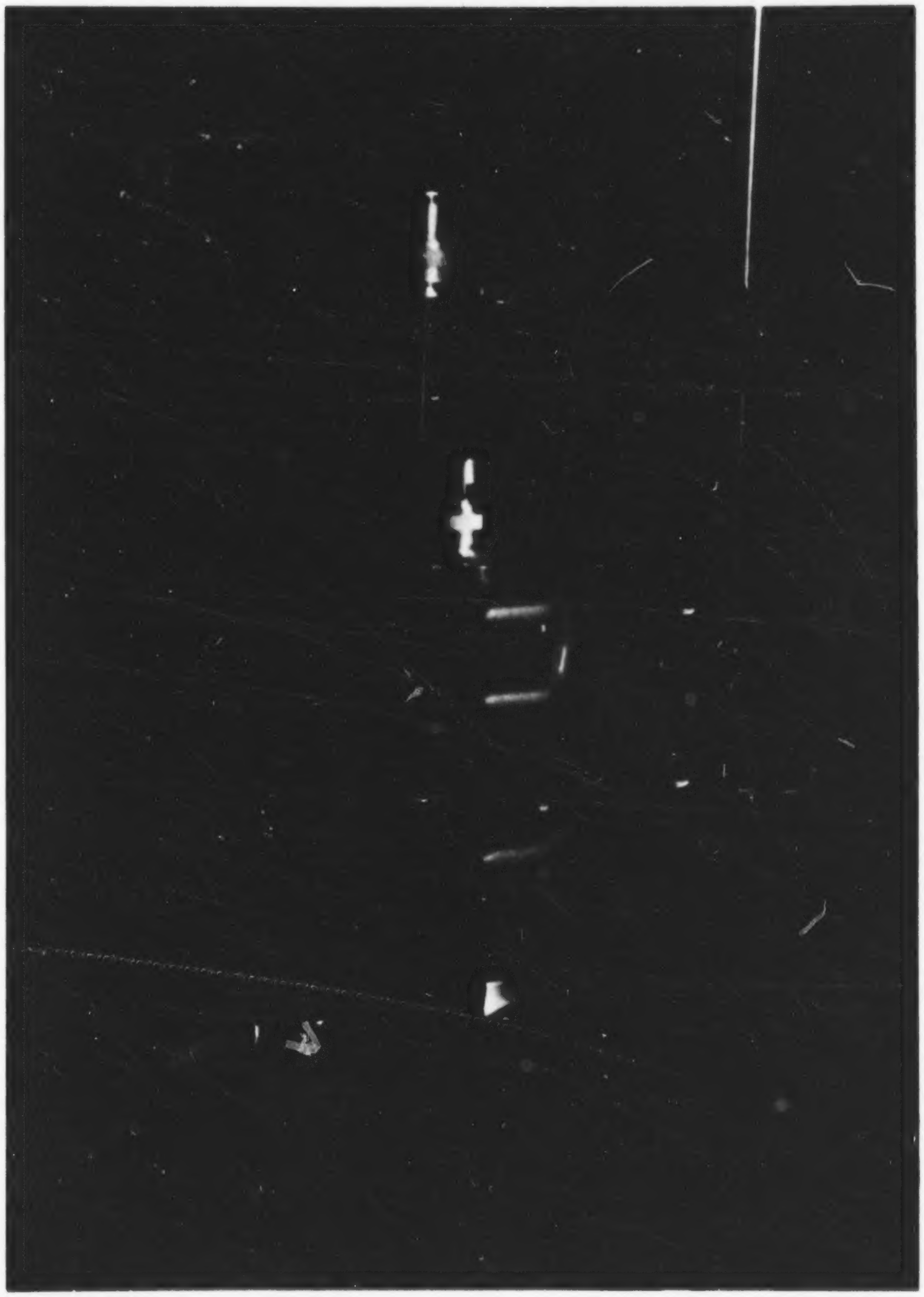


Figure 1.1.1-2 Alpha scintillation counter — zinc sulfide screen

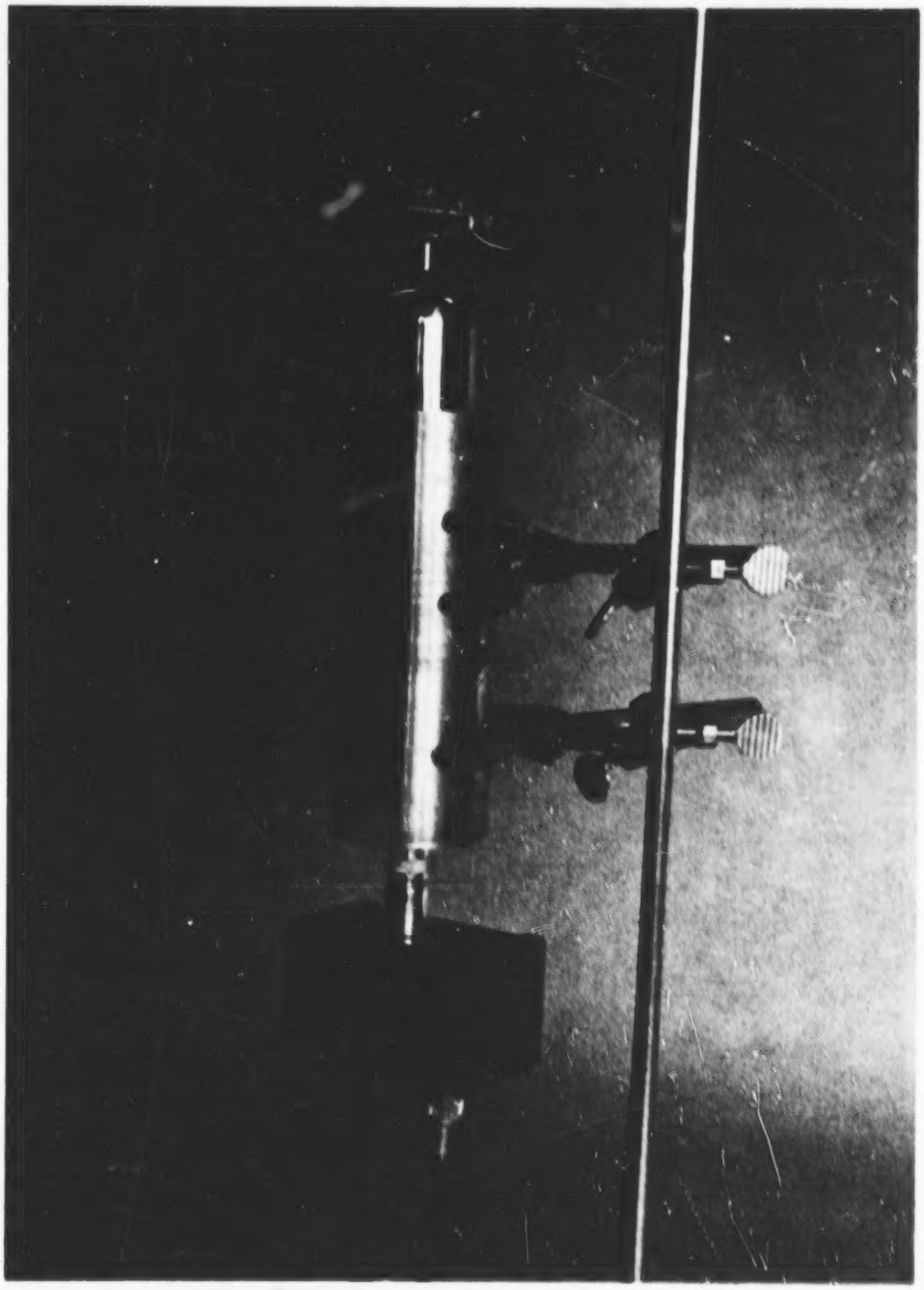


Figure 1.1.1-3 Typical radon counter

1.1.2 Beta Activity

Beta particles are negatively charged electrons ejected from the nucleus when a neutron decays to a proton and an electron. They are not monoenergetic, but have a continuous distribution of energies from zero up to E_{max}, the maximum value reported for the particular radioisotope. Each radionuclide has a different decay scheme which can be used to help identify the constituents of a sample containing beta emitters. Some beta emitters have many E_{max} values due to the way the atom reaches a stable state. The average energy of the beta particles from a given emitter is generally taken to be about one third of the maximum. The energy released by decay partially determines the type of instrument needed.

For each instrument described, there is an operating high voltage plateau which will yield consistent counting results. To determine this voltage range, counts are made with a beta emitter which has approximately the same beta energy as the beta emitter in the samples. Counts are made at 50-volt increments. When the counts from one 50-volt increment to the next are within 1 percent of each other, the plateau has been reached and the operating voltage lies in this plateau. Each instrument varies as to the length of the plateau and the best operating voltage. The operating voltage is influenced by the construction of the counter and for a gas ionization detector, the type of gas used. Additional information will be found in the operating manual supplied with the particular instrument and in several references listed at the end of this Section.

Calibration of beta counters is discussed in 1.3 RADIOACTIVE STANDARDS. 1.4.1 describes performance standards which must be used daily to assure that the counter is functioning as it was when calibrated.

For counting low-level activities, the count rate of the counter with no sample present (the background count) must be accurately known. Consult 1.4.2 Background Control for additional information.

GEIGER-MUELLER COUNTER

Application

The Geiger-Mueller (GM) counter is a gas ionization detector operated in the Geiger-Mueller region of response. In this application, the gas ionization chamber is called a GM tube. The cathode of this tube is usually a part of its wall, and the anode is a central wire mounted within the cathode. GM tubes contain the counting gas, which is usually a noble gas mixed with a small percentage of some halogen or organic gas to provide quenching. Typical gas mixtures are argon and ethanol, helium and isobutane, and neon and an organic halide.

The GM counter is relatively inexpensive, can be used with very simple rate meters and scalers, has a very low threshold of sensitivity, and is relatively trouble-free. Its high background, low counting efficiency, and inability to differentiate between two or more types of incident radiation can be disadvantageous in some applications.

The National Center for Radiological Health uses the GM detector to count samples containing near-tracer levels of activity. Although all pulses produced in the GM tube are the same size whether they originate from a low or high energy beta particle, qualitative identification of beta emitters in samples of high enough activity can be obtained by placing various thicknesses of aluminum absorbers between the sample and the GM tube. In this manner, the endpoint energy, or E_{max}, of the beta emissions from the source can be determined.

Almost any planchet is suitable for the GM detector, and reproducible results will be obtained as long as the planchet diameter is smaller than the diameter of the GM tube itself. In a 1½-inch thick lead shield, a 1½-inch diameter tube will have a background of about 30 counts per minute. If the radioactive material is near the edge of a 2-inch diameter planchet, the counting efficiency is less than if the same activity is deposited near the center. Since the sealing window must have a density thickness of about 2 milligrams per square centimeter, and there is an air path between the sample and window, there is a substantial absorption loss for beta energies less than 400 Kev (E_{max}).

Operation

The counting efficiency of this instrument is the lowest of those described here, especially for low-energy beta particles, because of the relatively thick window and poor geometry. Significant dead-time losses can occur if the count rate is high (above 10,000 counts per minute) and will usually be a problem only when the instrument is being calibrated at high levels of activity. If sample count rates are excessive, the sample must be counted at a greater distance from the tube. Normal losses due to dead-time are 0.5 percent per 1,000 counts per minute.

A plateau should be obtained at regular intervals to ensure that the GM detector is functioning properly. The plateau should not have a slope of more than 2 percent per 100 volts, and for a new tube should be about 250 volts long. As the tube ages, the plateau will shorten. The operating voltage should be chosen at the lower third of the plateau to prolong the life of the tube. Each tube has its own voltage requirement, but most operate at voltages of less than 2,000.

Once this operating voltage has been determined, the tube should be checked against a performance standard at least three times each day — in the morning, around noon, and at the close of the working day. Background measurements should be made at least twice a day.

Each Geiger-Mueller counter, illustrated in Figure 1.1.2-1, will be accompanied by an operating manual when purchased. It should be consulted for more specific information on calibration and operation of the counter.

INTERNAL PROPORTIONAL BETA COUNTER

Application

The internal proportional counter, previously discussed under 1.1.1 Alpha Activity, is also useful for measuring gross beta activity, where count rates are apt to be higher than in samples chemically separated to contain a single beta-emitting nuclide. It can be a satisfactory instrument for measuring levels of beta activity as low as 5 picocuries per sample if long counting times are used. Even weak beta emitters can be counted, because the sample is within the counter itself. The detector has 2-pi geometry, and counting efficiency can be as high as 75 percent because of backscatter from the planchet. The increased backscatter is a function of beta energy and of the atomic number of the planchet material.

When beta activity of a sample containing both alpha and beta emitters is to be measured, care must be taken to subtract the count contributed by the alpha emitters from the total count obtained at the beta plateau. The gamma counting efficiency is very low, ranging from approximately 1 percent for 1.0 Mev gammas to approximately 5 percent for 0.1 Mev gammas, and any contribution from gamma emissions can usually be neglected.

Operation

When the internal proportional counter is operated at approximately 1,800 volts, it becomes a beta counter, although alpha and gamma radiations are also counted. There are therefore two plateaus, one for alpha and one for alpha plus beta-gamma emissions. The efficiency for counting alpha activity at voltages in the beta-gamma plateau is somewhat higher than that obtained at voltages in the alpha plateau. This ratio must be determined if the alpha count is to be subtracted from the beta-plus-alpha count to obtain the corrected beta activity.

The plateau is determined by counting an extended source (2-inch diameter) having approximately the same beta energy as the samples. The operating voltage should be chosen about midway on the beta-gamma plateau. The plateau should be checked at one-month intervals or whenever a new tank of gas is installed.

The background at the beta plateau of an unshielded chamber of 2¼-inch internal diameter is approximately 55 counts per minute and is about 30 counts per minute for one shielded with 2 inches of lead.

The counting efficiency is a function of energy, sample thickness, and backing material of the sample. Distribution of activity in the planchet is relatively unimportant, although the efficiency is somewhat lower at the edges of the dish. Table 1.1.2-1 shows typical efficiencies for counting radionuclides of various average beta energies in the internal proportional counter.

It is extremely important that the samples be conducting to ground to eliminate a static charge buildup which will produce sporadic and inconsistent counts. This static buildup can be compared to formation of a cloud over the sample. During cloud formation, the counts would be suppressed, and when the cloud is removed (discharged) a burst of counts would be observed. Therefore, a non-metal planchet such as polyethylene or glass cannot be used.

The manufacturer's operating manual should be consulted for additional information on operating characteristics and trouble shooting.

Table 1.1.2-1 Typical counting efficiencies of the internal proportional beta counter for weightless samples

RADIONUCLIDE	AVERAGE β ENERGY (Mev)	TOTAL EFFICIENCY (%)
^{95}Nb	0.046	52
^{147}Pm	0.062	58
^{131}I	0.180	65
^{36}Cl	0.252	70
^{137}Cs-^{137m}Ba	0.268	70
^{90}Sr-^{90}Y	0.566	73
^{89}Sr	0.589	73
^{91}Y	0.615	73
^{32}P	0.693	73
^{90}Y	0.931	73

Counting chamber diameter: 2¼ inches

Planchet dimensions: 2-inch diameter by ¼ inch high, 0.018-inch thick stainless steel

END-WINDOW PROPORTIONAL COUNTER

Application

End-window proportional counters have application for counting moderate to high activity levels and for samples that cannot be fixed well in the planchet or sample holder. Large counters of this type can be used to count high-volume air samples such as those collected on 8-inch by 10-inch glass fiber filters. A typical end-window proportional counter is shown in Figure 1.1.2-2.

The end-window instrument is less sensitive than the internal proportional counter because of poorer sample geometry and because of absorption losses in the air path and window. Although a very thin window can be utilized for alpha counting, it is not particularly recommended because of the end-window detector's poor efficiency for alpha detection. It can be used as a screening instrument for alpha and low-energy beta emitters, but it is unsuitable for quantitative measurement of these emitters.

Almost any type of planchet can be used with the end-window counter, but for reproducible results its diameter must be somewhat shorter than that of the window. There is no problem of static charge buildup because the sample is external to the counter.

Operation

The end-window proportional counter operates on essentially the same principle as the internal proportional counter. The detector ordinarily uses P-10 gas (argon-methane mixture).

Counting efficiency of the end-window proportional counter is little more than half that of the internal proportional counter. Again, this is due to absorption of some beta particles in the air path and in the window material. The lower energy betas (E_{max} less than 300 Kev) and the back-scattered events are especially attenuated.

Background is lower than that of the internal proportional counter because there is less detector area. Contamination is not as apt to occur because the sample is external to the counter. Background counts need be taken only once or twice daily unless a sample contacts the window or contaminates the inside of the shield or sample holder.

Plateaus should be taken at the same intervals and for the same reasons as for the internal proportional counter. Additional information on operation or trouble shooting will be found in the manufacturer's operating manual.

LOW-BACKGROUND BETA COUNTER

Application

The low-background beta counter, illustrated in Figure 1.1.2-3, is designed for measuring low levels of activity. Its primary application is for the determination of strontium fission products in the environment, and use of the counter should be restricted to samples of low to moderate activity. It has the highest sensitivity of any common laboratory beta counter for samples mounted in counting dishes. The instrument is sensitive to about 0.5 picocurie per sample for energetic beta-emitters counted 100 minutes or more. It is possible to determine activity levels of less than one picocurie per sample for the energetic strontium beta emitters. For betas having E_{max} less than 0.3 Mev, other counters should be considered.

The counting dish can be of almost any material depending on the chemical procedure required for sample preparation. The diameter of the dish should be smaller than the diameter of the counter to obtain reproducible results. The two most commonly used planchets are the stainless steel dishes and the nylon ring and disk types, which are pictured in Figure 1.1.2-5. For some applications, the nylon ring and disk offers the advantage of producing a more uniform sample and is easier to prepare. A thin Mylar cover is placed over the sample to eliminate loss of sample and to prevent contamination of the counting chamber. The absence of a wall on the planchet and the protective cover over the sample allows the samples to be placed closer to the window of the counter, thereby yielding higher counting efficiencies. Table 1.1.2-2 lists typical counting efficiencies obtained from samples mounted in the nylon ring and disk assembly.

Operation

A low-background beta counter is shielded by two inches of lead or equivalent to stop external gamma rays, and by coincidence circuitry to reduce the contribution from cosmic interactions in the shielding material. The circuitry consists of one or more guard detectors placed over the central detector(s) so that any radiation interacting in both the guard and central detector(s) is not recorded as a count.

The detectors are commonly GM end-window tubes with thin windows (less than 0.1 milligram per square centimeter) and a positive gas pressure maintained by a low purge rate. Sometimes P-10 gas (argon-methane mixture) is used, and the counter is then operated as a proportional counter. However, the detector is usually operated in the Geiger-Mueller region, using helium-isobutane as the gas, where the pulses produced are very large and no additional amplification is required. The system is usually packaged as a complete unit of central detector, guard tubes, shielding, and scaler. The scaler will have the required high voltage and separate registers for the central detector(s) and guard tube(s).

The counting efficiency for yttrium 90 distributed uniformly on a 2-inch stainless steel planchet placed close to a 2¼-inch detector, is about 42 percent, and is about 50 percent for the nylon ring and disk mount. A lower efficiency is obtained for beta-emitters of lower energy, as shown in Table 1.1.2-2.

For samples having activity levels of less than 5 picocuries per sample, adequate counting times in these instruments are usually 100 minutes or overnight. Background measurements must be made at least once daily for 100 minutes or more. In the Geiger-Mueller mode of operation the background count rate should be about 1 count per minute for a 2-inch diameter tube. When the detector is operated in the proportional mode, the background count rate can be further reduced by use of discriminators.

Table 1.1.2-2 Typical total counting efficiencies for the low-background beta counter

Efficiencies for weightless samples on a 1-inch diameter nylon ring and disk mount*

RADIONUCLIDE	AVERAGE β ENERGY (Mev)	TOTAL EFFICIENCY (% ± 5%)
^{90}Sr	0.200	46
^{137}Cs-^{137m}Ba	0.268	43
^{90}Sr-^{90}Y	0.566	50
^{89}Sr	0.589	50
^{90}Y	0.931	53

Efficiency equations for samples of various density thicknesses on a 1-inch diameter nylon ring and disk mount*

RADIONUCLIDE	EFFICIENCY (log Y), WHERE X = mg/cm^2
^{90}Sr	$\log Y = 1.66652 - 0.002101\ X$
^{137}Cs-^{137m}Ba	$\log Y = 1.63556 - 0.0022726\ X$
^{90}Sr-^{90}Y	$\log Y = 1.69607 - 0.00119\ X$
^{89}Sr	$\log Y = 1.69669 - 0.0007374\ X$
^{90}Y	$\log Y = 1.72415 - 0.0003951\ X$

* the nylon ring and disk mounts have an active area of 3.9 cm^2

LIQUID SCINTILLATION COUNTER

Application

This instrument is particularly well suited to counting low-energy beta emitters such as tritium or carbon 14. By mixing the sample with the liquid scintillation medium, self-absorption losses are eliminated. Counting efficiency can approach 100 percent for high-energy beta emissions, but for those of carbon 14 and tritium the efficiency is much less. Use of the liquid scintillation counter is not limited to counting low-energy beta emitters, but it or a method equivalent to it, such as gas phase counting, is essential for counting weak beta emitters with reliability.

Early models required placing the phototubes in a freezer to reduce the dark current noise to an acceptable level. Recent improvements, however, make this unnecessary for all but the lowest levels of activity (less than about 30 picocuries per sample for ^{14}C).

Operation

In a liquid scintillation counter, the samples and scintillator form a homogeneous mixture in solvents such as toluene, xylene, and 1,4-dioxane. Light flashes produced in the mixture are detected and amplified by the photomultiplier tube.

The samples are placed into a transparent or translucent bottle to enable the light to be transmitted to the phototubes. As in any other counter, the calibration standard must contain the same radionuclide prepared in the same medium. The background count rate is determined by counting the activity of a bottle containing both solvent and scintillator, since this mixture is the sensor and a slight amount of activity may be present in the material itself. Background counts should be taken at least once each day.

Most of the liquid scintillation counting systems designed for low level counting place two phototubes in coincidence. Only one is considered the detector, and it is connected to the analyzer. When both tubes receive a pulse simultaneously, a count is registered equivalent to the energy of the radiation absorbed. When only one tube sees the pulse, no count is recorded. In this way the dark current, or photomultiplier background, is practically eliminated. A discriminator is used to eliminate additional low-energy pulses, but the weaker pulses from soft betas are also eliminated, thereby reducing the counting efficiency for these emissions.

The beta energy of the nuclide to be counted determines the discriminator setting and window width. Window width is also dependent on whether or not there is more than one beta emitter present.

Most liquid scintillation counters are coupled to an analyzer with at least two channels. This enables more than one beta emitter to be analyzed at the same time as long as their E_{max} values differ by at least a factor of three.

More detailed information on operation of the liquid scintillation counter will be found in the manufacturer's instruction manual. An example of such a counter is shown in Figure 1.1.2-4. Typical counting vials are also shown in Figure 1.1.2-5.

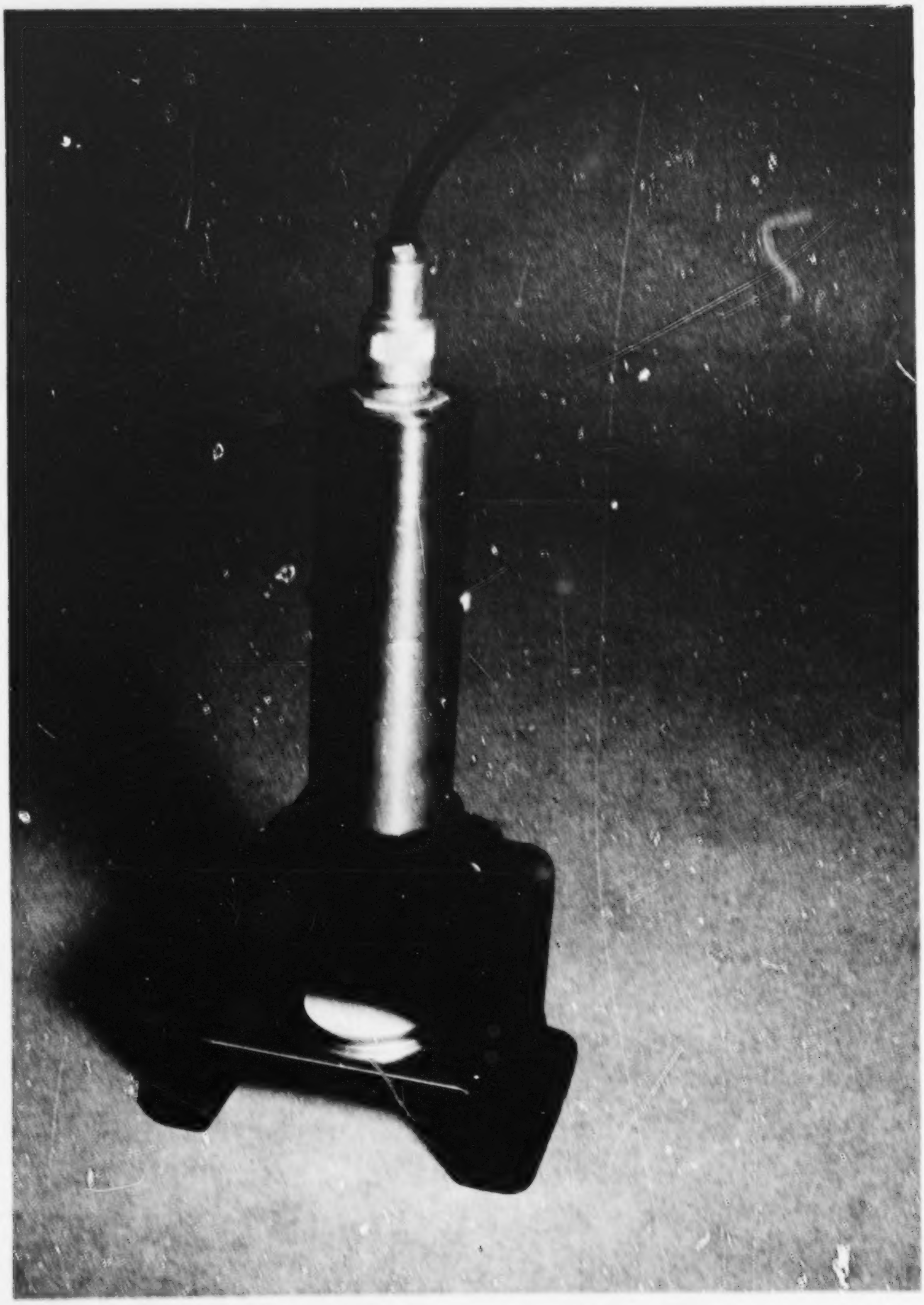


Figure 1.1.2-1 Typical Geiger-Mueller counter

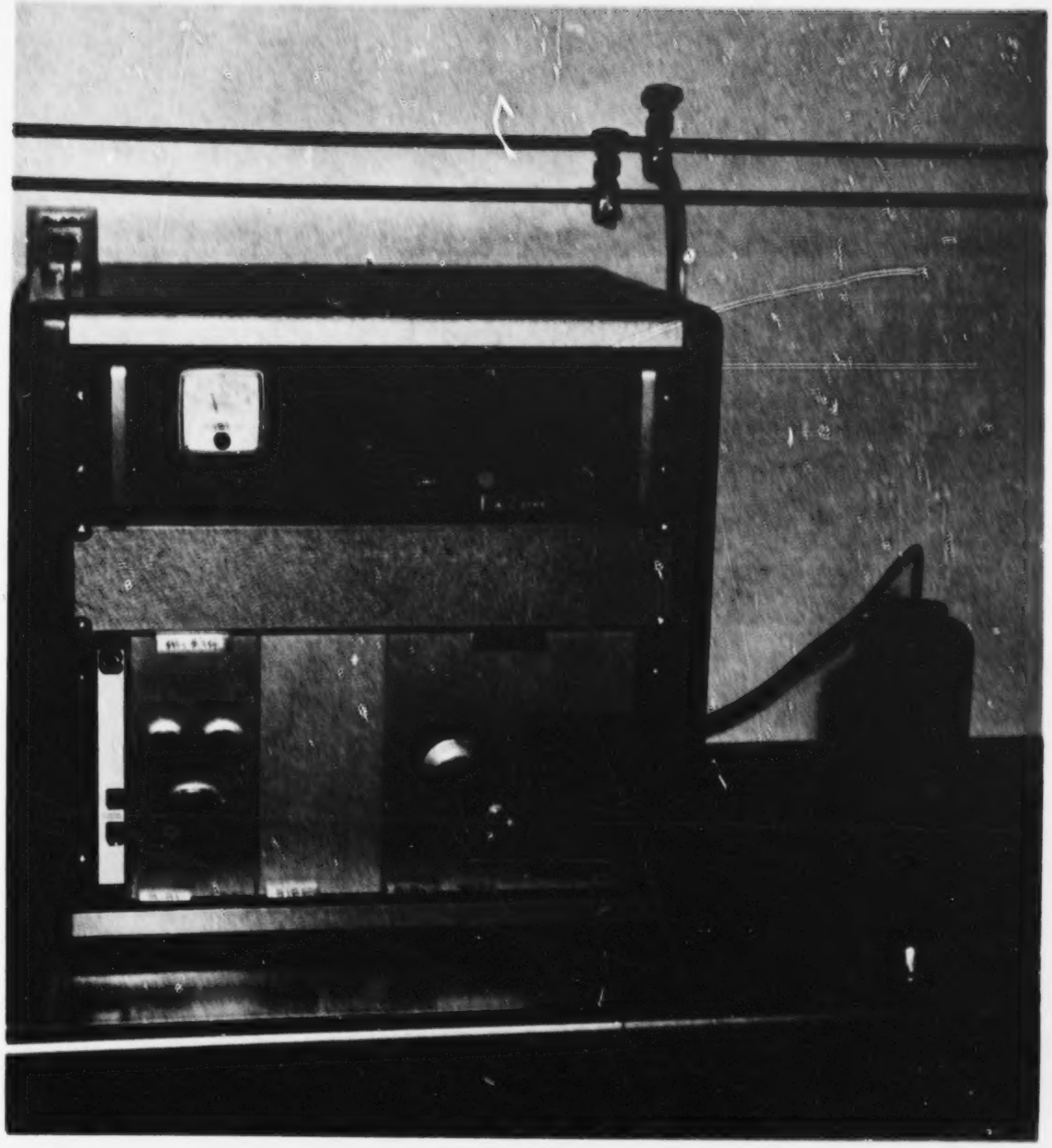


Figure 1.1.2-2 Typical end-window proportional counter

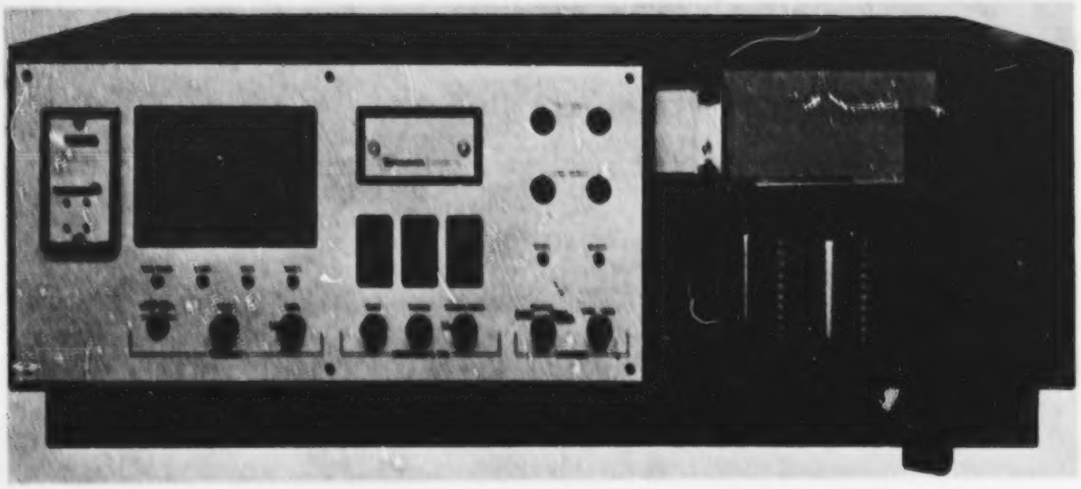


Figure 1.1.2-3 Low-background beta counter

Photograph courtesy of Beckman Instruments Inc.
Scientific and Process Instruments Division,
Fullerton, California.

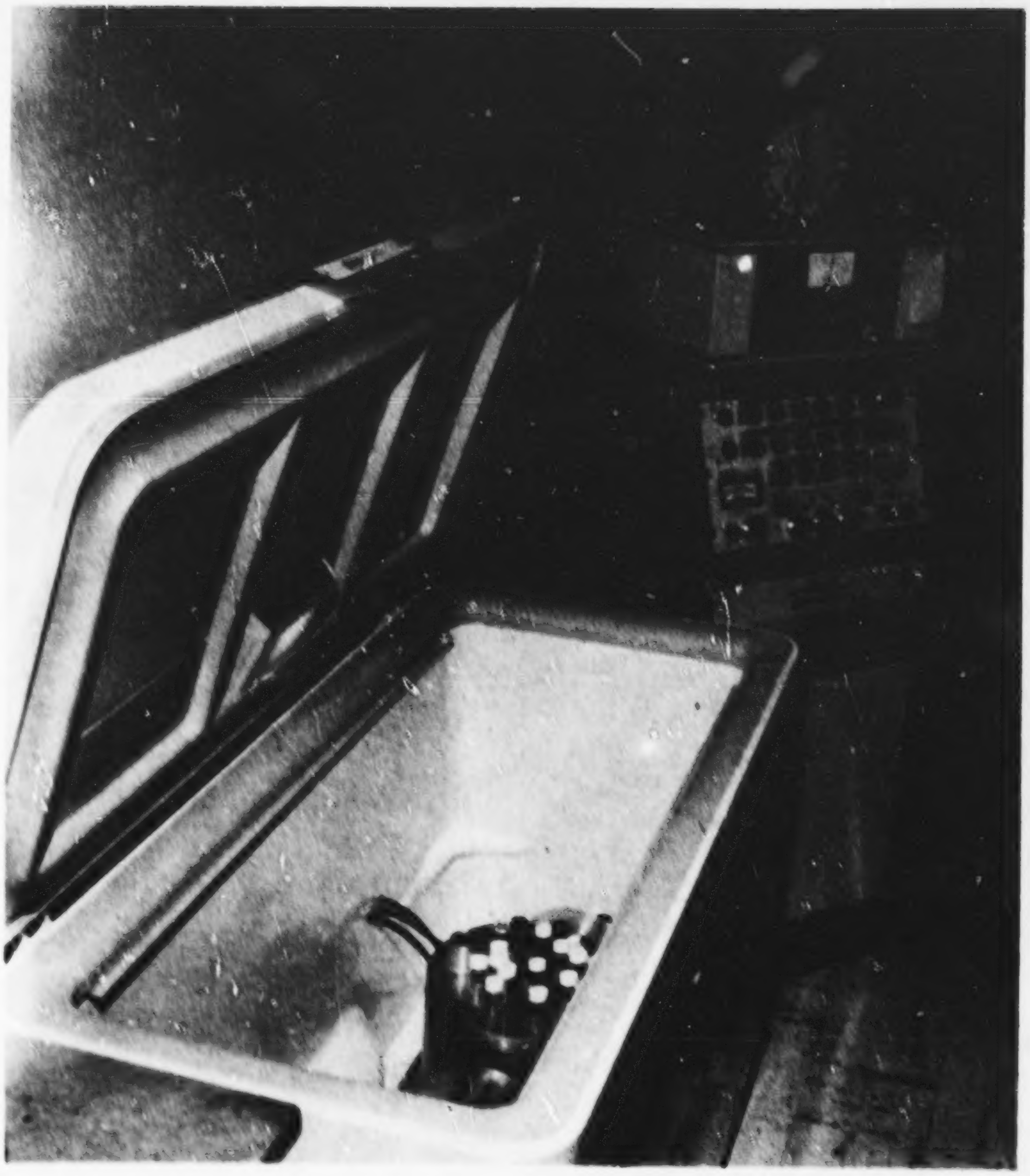


Figure 1.1.2-4 Liquid scintillation counter

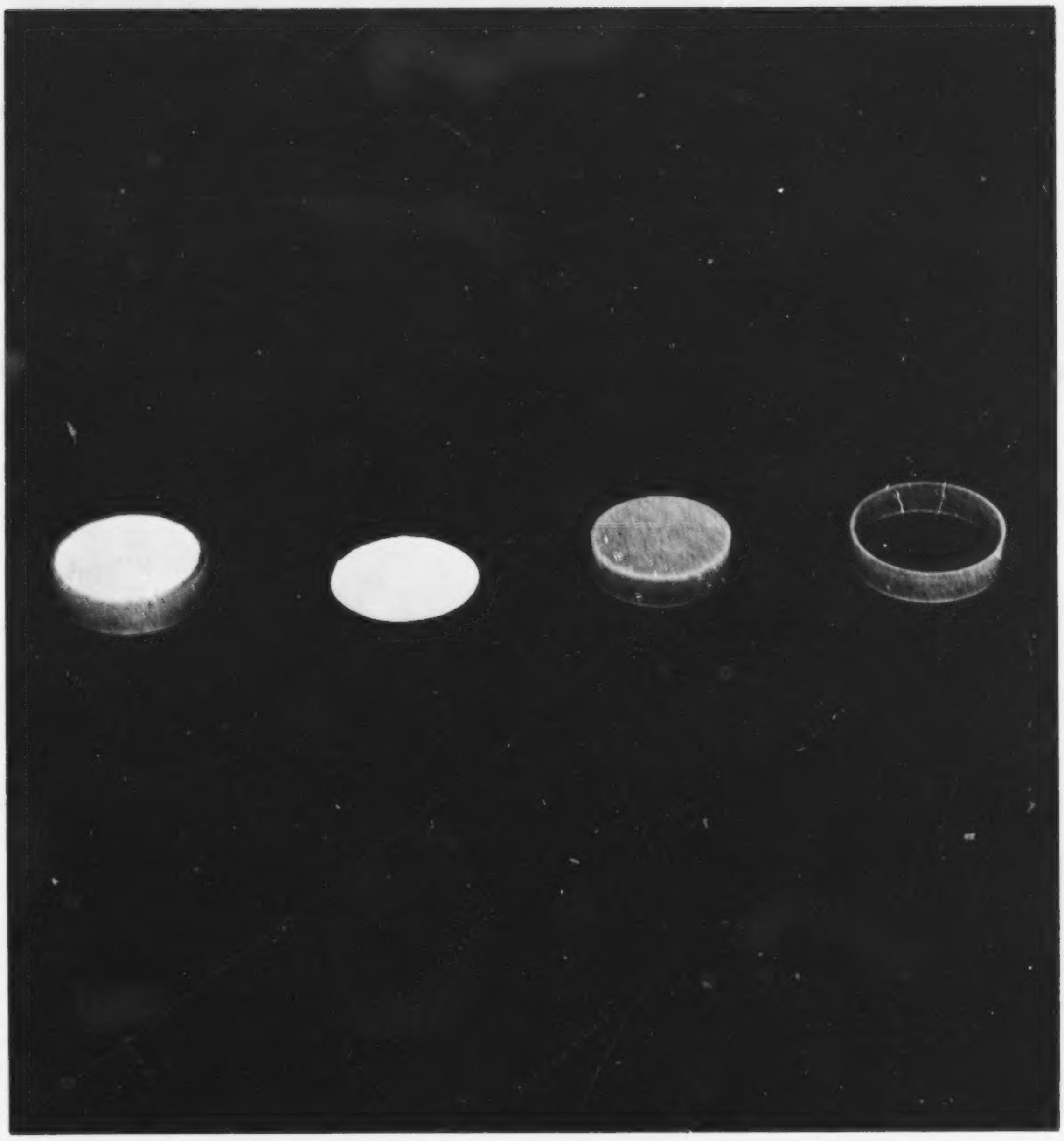


Figure 1.1.2-5 Sample holders for beta counting

1.1.3 Gamma Activity

Gamma rays are electromagnetic radiations emitted by the nucleus as photons of discrete energies. The photons have no mass and have high penetrating power. Therefore, sample preparation is generally much less of a problem for counting gamma emitters than for counting either alpha or beta emitters.

The method for measuring gamma activity is basically to capture part or all of the energy released through decay, and to convert it into a current flow or pulse which can be recorded. The gross count can be taken by totaling the pulses recorded on scalers. For spectral analysis, the pulses are sorted out by energy, and the number of pulses counted in each energy band is stored separately. A pulse height analyzer is used for this spectral analysis.

GROSS GAMMA COUNTER

Application

A gross gamma counter is frequently used as a screening device to provide a rapid means of selecting from a group of environmental samples those which have a relatively high activity. It is also used in tracer experiments where a known radionuclide is to be counted, as in determining chemical yield for an analytical procedure by use of a tracer. Depending on the type of sample to be counted, a solid or a well crystal detector can be used for these applications.

Operation

A relatively small crystal scintillator, such as a 2-inch by 2-inch right cylinder, is frequently used for gross gamma counting because total absorption of the gamma rays is not necessary. Any partial interaction with the crystal which produces a pulse above the threshold will register as a count. Shielding is desirable, but it need not be massive. About 1 inch to 1-1/2 inches of lead, or equivalent, is adequate for most applications. With this amount of shielding, a 2-inch by 2-inch crystal will have a background of approximately 300 counts per minute. Such a shield is shown with the gross gamma counter in Figure 1.1.3-1. A more massive, gun-barrel shield containing a 4-inch by 4-inch right cylindrical sodium iodide crystal is also shown.

A photomultiplier tube detects the light flashes produced in the crystal scintillator. The output from this tube is coupled to a scaler having an amplifier, or an amplifier is inserted as a separate component. Although a simple scaler may be adequate, low-energy sources in particular may require a relatively stable high voltage supply.

The gross gamma counter is the simplest and cheapest of the gamma counters routinely used in the laboratory. Its principal limitations are that it has no energy discrimination and that its relatively high background makes it useful only for samples of fairly high activity.

As for all gamma counting, gross gamma counting requires minimal sample preparation because self-absorption losses are not a major problem. For the same reason, almost any sample configuration can be used. It is important, however, to maintain a constant geometrical configuration for a given sample type and to calibrate with a standard having the same configuration as the sample. Even where only relative counts are needed, as for checking chemical procedures, the geometry must be kept constant for all count rates being compared, or it must be calibrated for a variety of sample sizes and configurations.

For most gamma measurements, a discriminator should be used to eliminate much of the low-energy component of background. An optimum setting can be obtained by taking counts at various discriminator settings, both from background and from a source. The best discriminator setting for a given gamma energy is the setting at which the highest value of the ratio S^2/B is obtained, where S is the sample count rate and B is the background count rate.

Gross gamma counting efficiencies vary with energy, but they are quite high because only a partial interaction is needed. For spectrometry, however, total interaction of the gamma photon is needed if the pulse is to be recorded under the photopeak.

Background should be measured twice daily or more often if high activity sources are being moved about nearby. A change in position of these sources will affect the background.

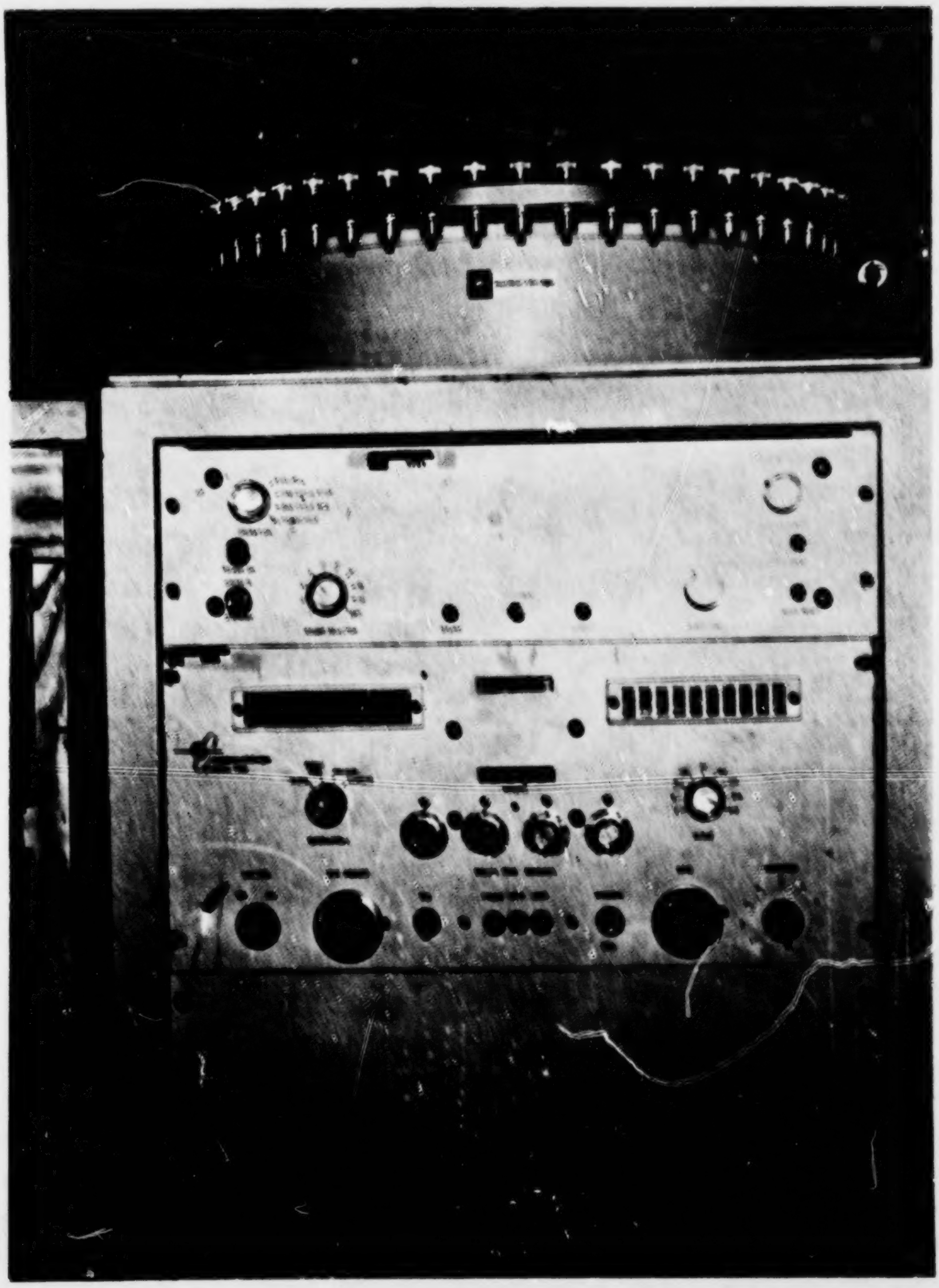


Figure 1.1.3-1 Gross gamma counter

GAMMA SPECTROMETER

Application

Gamma spectrometry is used extensively to identify radionuclides. The spectrometer becomes a quantitative tool with suitable calibration and background data accompanied by measurement of spectral interferences. Self-absorption losses are negligible, so large-volume samples can be scanned with little or no prior preparation.

The spectrometers are pulse height analyzers of the single-channel or multichannel type. A pulse height analyzer sorts pulses according to energy expended in the detector. The multichannel analyzer simultaneously sorts and records pulses falling in many different energy bands or increments in a given time interval. For a given analyzer, the total energy range scanned is divided into equal increments called channels. The single channel analyzer detects and records pulses in only one energy band at a time. The single-channel analyzer is adequate for counting tracer levels of activity, but for low activity samples, the multichannel analyzer is essential because of the excessive counting time required to cover a spectrum channel by channel with a single-channel analyzer.

Either a 3-inch by 3-inch or 4-inch by 4-inch right cylindrical thallium-activated sodium iodide [NaI(Tl)] crystal provides optimum sensitivity for gamma energies up to 2 MeV(5,6). These sizes are therefore used for environmental samples containing fallout debris and natural radioactivity. For low-activity gamma spectrometry, the phototube base should be removed and a mu-metal cover should shield the tube to prevent magnetic fields from distorting the spectra.

Low-energy gamma spectrometry ($E_\gamma < 150$ keV) requires a very thin crystal less than 0.5 inches thick enclosed by a thin protective can. This thin crystal can also be used to detect the X rays emitted by some radionuclides to help identify the components of a sample spectrum. Very high-energy gamma photons ($E_\gamma > 2$ MeV) are not seen efficiently by the thin detector. Since the predominant gamma energies of gamma emitters in most environmental samples are less than 2 MeV, larger crystals will not be discussed.

Typical gamma spectrometers or pulse height analyzer systems are illustrated in Figure 1.1.3-2. Several sample containers routinely used

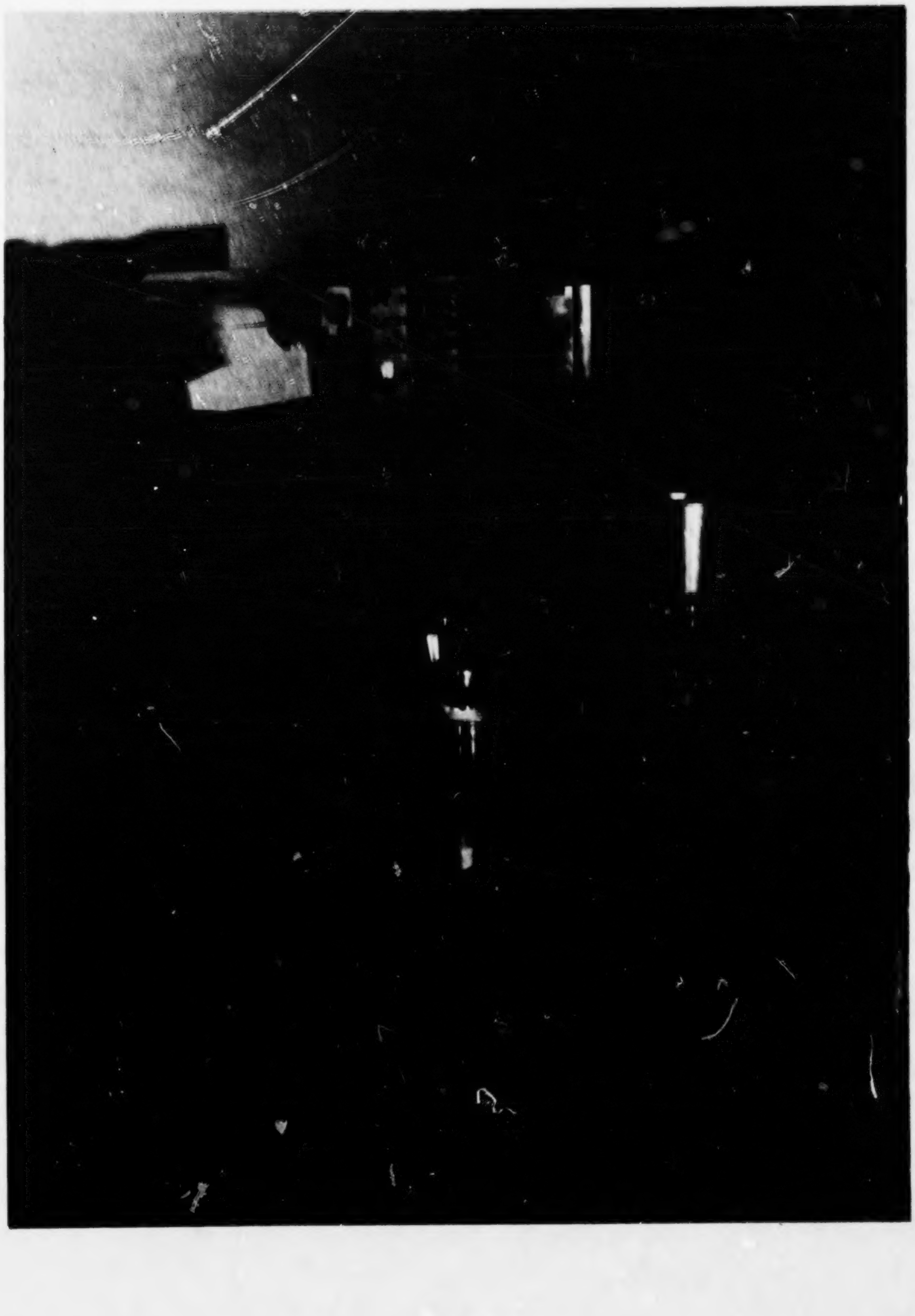


Figure 1.1.3-2 Gamma spectrometer and sample container

by the National Center's laboratories for counting and analyzing gamma emitters are also shown.

The Crystal Detector

The detector for most gamma spectrometer systems is a sodium iodide crystal optically coupled to a photomultiplier tube. The tube is connected into the analyzer through a pre-amplifier and linear amplifier. The analyzer records each pulse in its proper channel or energy increment. Each channel represents a certain amount of energy absorbed in the crystal. The spectrum shows a characteristic photopeak at the full energy of the gamma ray, and at lower energy regions shows counts which arise from partial interactions of the gamma rays with the crystal. By knowing the decay schemes of radionuclides, it is possible to identify specific isotopes by their gamma energies.

Crystal size is very important in gamma spectrometry. If too large a crystal for the application is chosen, the background will be unnecessarily high. If a crystal is too small for the energies being scanned, the photopeak counting efficiency will be low because few of the gamma photons will expend their full energy in the crystal. The detector is energy dependent, the efficiency being lower for higher energies. This is especially noticeable in pulse height analysis, because the entire photon energy must be spent in the crystal to be recorded under the photopeak. This type of interaction is called photoelectric, and it is the most important interaction in gamma spectrometry.

All higher energy photons contribute to a lower region of the energy spectrum because of Compton interaction. In the Compton interaction, only a portion of the total energy is absorbed in the crystal and the remainder is scattered out of the crystal. The energy absorbed is recorded as a pulse in a channel below that of the photopeak. The amount of energy lost by this process is somewhat energy dependent, but it can be from almost full energy to only a small percentage of the total energy of the gamma photon. Frequently there are multiple Compton interactions, and if they occur in the crystal, the total energy absorbed will be additive. In some instances, the sum may equal the full gamma energy of the photon, and the pulse will then be recorded under the photopeak.

Another form of gamma interaction important to gamma spectrometry is pair production. This process occurs only at gamma energies above 1.02 MeV.

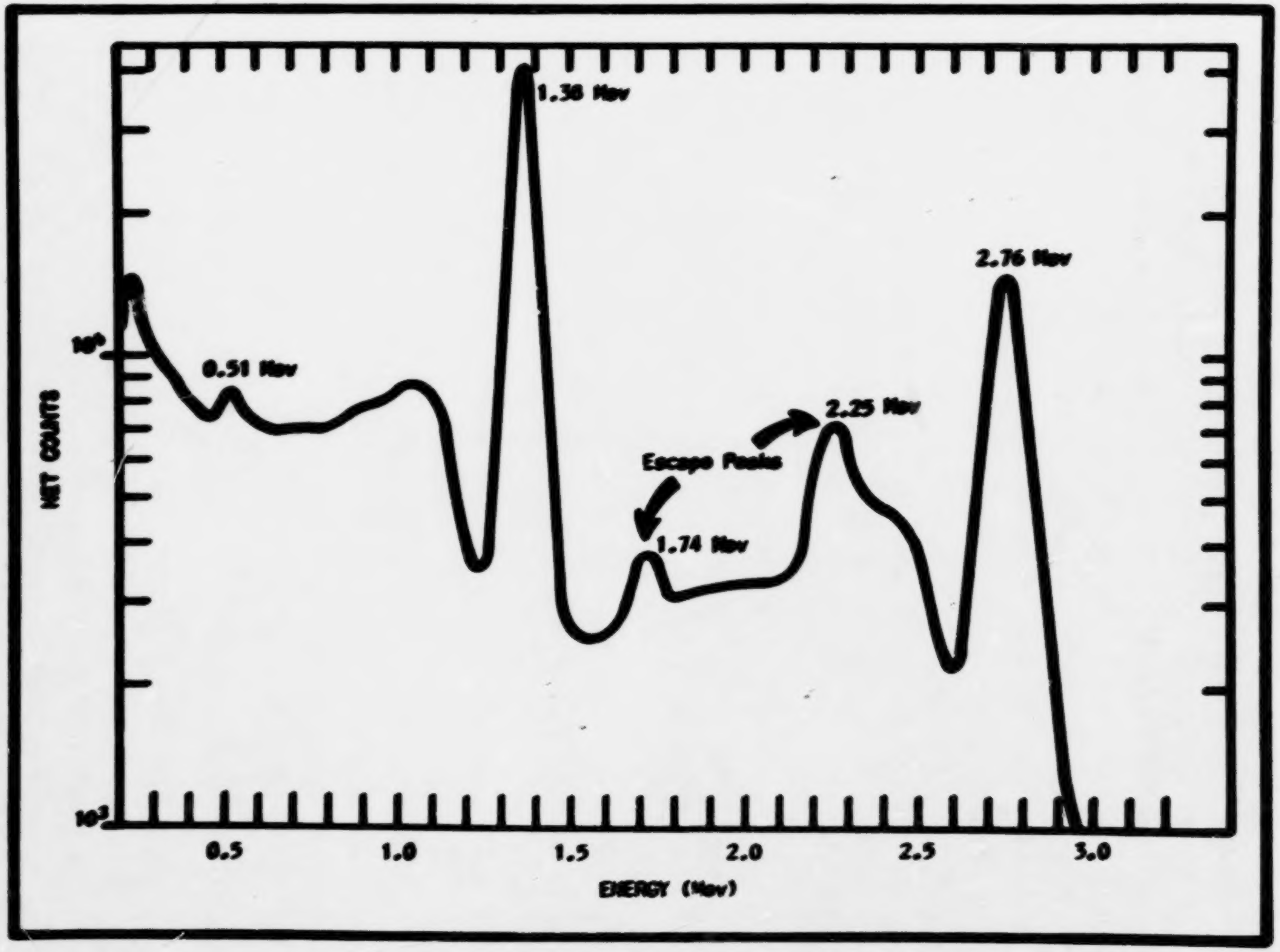


Figure 1.1.3-3 Gamma spectrum of sodium 24 on a 4-inch by 4-inch sodium iodide crystal

One electron of the pair is negatively charged, and the other positively. The positively charged electron, or positron, is slowed down until it interacts with a negatively charged electron and both are annihilated. Their rest mass energy of 1.02 MeV is converted to two photons, each having an energy of 0.51 MeV, which are emitted in opposite directions.

This conversion results in a peak in the gamma spectrum at 0.51 MeV. If the counting geometry is such that both of the photons can interact with the detector simultaneously (as in a well-type detector), a sum peak at 1.02 MeV will be observed. If, however, one or both entirely escape the detector, there will be peaks observed at energies of 0.51 or 1.02 MeV less than the full energy of the photon. The gamma spectrum of sodium 24 in Figure 1.1.3-3 illustrates this phenomenon.

Counting Efficiency

Total counting efficiency values obtained for various radionuclides in the calibration of a typical spectrometer with a 4-inch by 4-inch sodium iodide crystal detector are presented in Table 1.1.3-1. The radionuclides, in aqueous solution, were scanned in several volumes and in the geometric configurations represented by a 3.5-liter aluminum Marinelli beaker, a 1-pint "cottage cheese" container, and a 4-ounce plastic container.

The term "total efficiency" denotes the ratio of the net gamma counts observed in a peak spectral region to the total number of disintegrations of the radionuclide of interest in the same period of time, and is determined by the following equation.

$$\text{total efficiency (\%)} = \frac{\text{observed counts in peak region} - \text{background in peak region}}{\text{total disintegrations}} \times 100$$

If the activity of a standard is given in terms of total disintegration rate, the gamma abundance is not needed to determine the photopeak efficiency of a particular radionuclide. A radioactive standard of ruthenium 106 — rhodium 106 (^{106}Ru—^{106}Rh) will serve as an example. Let the following information be given:

^{106}Ru activity in the sample = 100,000 dpm

^{106}Rh (daughter of ^{106}Ru) gamma energy = 0.51 MeV

Abundance of the 0.51 MeV gamma of ^{106}Rh = 20%

Net gamma count rate between 0.44 and 0.56 MeV = 2000 cpm

The equation can then be written in one of three ways:

1) $$^{106}\text{Ru or }^{106}\text{Rh Eff. (\%)} = \frac{\text{net cpm in peak region}}{\text{dpm in sample of }^{106}\text{Ru or }^{106}\text{Rh}} \times 100$$

$$= \frac{2{,}000}{100{,}000} \times 100$$

$$= 2\%$$

2) $$^{106}\text{Ru-}^{106}\text{Rh Eff. (\%)} = \frac{\text{net cpm in peak region}}{\text{dpm in sample of }^{106}\text{Ru-}^{106}\text{Rh}} \times 100$$

$$= \frac{2{,}000}{200{,}000} \times 100$$

$$= 1\%$$

3) $$0.51\text{ MeV Eff. (\%)} = \frac{\text{net cpm in peak region}}{\text{dpm in sample} \times \text{gamma abundance}} \times 100$$

$$= \frac{2{,}000}{100{,}000 \times 0.20} \times 100$$

$$= 10\%$$

In the third case, the efficiency for the 0.51 MeV gamma photons would actually be less than 10% because the 2,000 counts in the photopeak region include Compton interactions from higher energy gamma emissions from ^{106}Rh.

Graphs of gamma efficiency plotted against gamma energy can be very useful if the gamma abundance values are accurately known and if the standard is precisely rated. If a range of gamma energies is obtained and the gamma abundances are known, it is possible to predict the gamma efficiency for an unknown radionuclide.

Resolution

Resolution is a measure of the sharpness of a photopeak and it determines the ability of a detector to separate or distinguish between the peaks of gamma rays having similar energies. Without good resolution, photopeaks of similar energies are difficult to quantify. Resolution is calculated by the following formula, which is illustrated in Figure 1.1.3-4. The units of energy can be either channel number or MeV, keV, etc. for

Table 1.1.3-1 Typical total counting efficiencies of a 4" by 4" NaI(Tl) crystal for several radionuclides

RADIONUCLIDE	ENERGY BAND (MeV)	PHOTON ENERGY (MeV)	ABUNDANCE (%)	HALF-LIFE	TOTAL COUNTING EFFICIENCY (%)* MARINELLI BEAKER 3.5 liter	PINT CONTAINER 450 ml	40 ml	4-OUNCE CONTAINER 7 ml
^{7}Be	0.39–0.53	0.48	11	53.5 d	--	0.82	1.7	--
^{22}Na	1.21–1.35	1.28	100	2.57 y	--	2.6	--	--
^{24}Na	1.27–1.45	1.37	100	15.0 h	--	3.1	5.6	--
^{40}K	1.39–1.53	1.46	11	1.27×10^{9} y	0.27	0.29	0.57	0.71
^{42}K	1.43–1.61	1.53	20	12.5 h	--	0.53	1.1	--
^{46}Sc	0.81–0.95	0.89	100	84 d	3.8	4.4	9.0	11.0
^{51}Cr	0.27–0.37	0.32	8	27.8 d	0.77	0.84	1.7	2.3
^{54}Mn	0.75–0.89	0.84	100	314 d	3.9	4.5	9.2	11.6
^{57}Co	0.07–0.19	0.12, 0.14	88, 10	267 d	--	15.5	28.4	--
^{59}Fe	1.03–1.17	1.10	56	45 d	2.0	2.2	4.5	5.6
^{60}Co	1.25–1.39	1.33	100	5.27 y	2.6	2.9	5.7	7.1
^{65}Zn	1.03–1.17	1.11	51	245 d	1.4	1.7	3.4	4.3
^{76}As	0.49–0.63	0.56	45	26.8 h	2.4	2.8	5.6	--
^{85}Sr	0.43–0.57	0.51	100	64 d	5.8	6.4	13.0	16.9
^{86}Rb	0.99–1.37	1.08	9	18.7 d	--	0.36	0.72	--

Table 1.1.3-1 Continued

RADIONUCLIDE	ENERGY BAND (MeV)	PHOTON ENERGY (MeV)	ABUNDANCE (%)	HALF-LIFE	TOTAL COUNTING EFFICIENCY (%)* MARINELLI BEAKER 3.5 liter	PINT CONTAINER 450 ml	40 ml	4-OUNCE CONTAINER 7 ml
^{88}Y	0.83–0.97	0.91	90	106 d	--	4.1	8.1	--
^{95}Zr–^{95}Nb	0.69–0.83	0.73, 0.76 (0.76)	98 (99)	65 d (35 d)	4.3	4.7	9.4	12.2
^{95}Nb	0.69–0.83	0.76	99	35 d	--	4.7	--	--
^{99}Mo–^{99m}Tc	0.09–0.19	(0.14)	(80)	67 h (6 h)	10.7	12.1	22.7	--
^{103}Ru	0.43–0.57	0.50	90	40 d	5.5	6.1	12.2	16.0
^{106}Ru	0.43–0.57	(0.51)	(20)	1.0 y	1.3	1.4	2.8	3.7
^{124}Sb	1.59–1.81	1.70	50	60 d	--	1.3	2.4	--
^{125}Sb	0.37–0.49	0.43	31	2.0 y	3.5	3.9	7.8	10.0
^{131}I	0.31–0.41	0.36	80	8.08 d	5.6	6.7	13.8	17.3
^{132}Te–^{132}I	0.51–0.29	0.23	95	78 h (2.3 h)	7.4	8.3	16.6	--
^{132}Cs	0.59–0.73	0.67	98	6.5 d	--	5.2	10.4	--
^{133}Ba	0.31–0.43	0.36	69	7.5 y	--	7.1	14.5	--
^{134}Cs	0.73–0.87	0.80	90	2.1 y	--	4.3	8.7	11.3
^{137}Cs	0.59–0.71	(0.66)	86	30 y	4.0	4.5	9.1	11.8
^{140}Ba	0.43–0.57	0.44, 0.54 (0.49), 5.26	(41)	12.8 d	5.5	6.0	11.1	13.5

Table 1.1.3-1 Continued

RADIONUCLIDE	ENERGY BAND (MeV)	PHOTON ENERGY (MeV)	ABUNDANCE (%)	HALF-LIFE	TOTAL COUNTING EFFICIENCY (%)*			
					MARINELLI BEAKER 3.5 liter	PINT CONTAINER 450 ml	40 ml	4-OUNCE CONTAINER 7 ml
^{140}La	1.49-1.71	1.60	88	40 h	2.6	3.0	5.2	--
^{141}Ce	0.09-0.19	0.15	49	33 d	6.2	7.0	13.4	16.0
^{144}Ce	0.09-0.19	0.13	10	185 d	1.5	2.0	4.1	4.6
^{147}Nd	0.45-0.59	0.53	15	11.1 d	--	0.93	1.9	--
^{198}Au	0.35-0.49	0.41	96	2.7 d	--	8.0	16.4	--
^{203}Hg	0.21-0.35	0.28	83	47 d	--	8.1	16.4	--
^{226}Ra	1.65-1.83	(1.76 and 1.78 ^{214}Bi)	(16, 3)	1600 y	--	0.64	--	--
^{232}Th	0.85-0.99	(0.91 ^{228}Ac)	--	1.4×10^{10} y	--	3.1	--	--

* Total counting efficiency is for the radionuclide (see Counting Efficiency) and is not the gamma efficiency

Note: The crystal was contained in a 0.019-inch thick stainless steel can. The radionuclide samples were in aqueous solutions. Efficiency values refer to total activity of parent and daughter when both are listed. Daughters, if present, are in equilibrium with parents at the time of calibration.

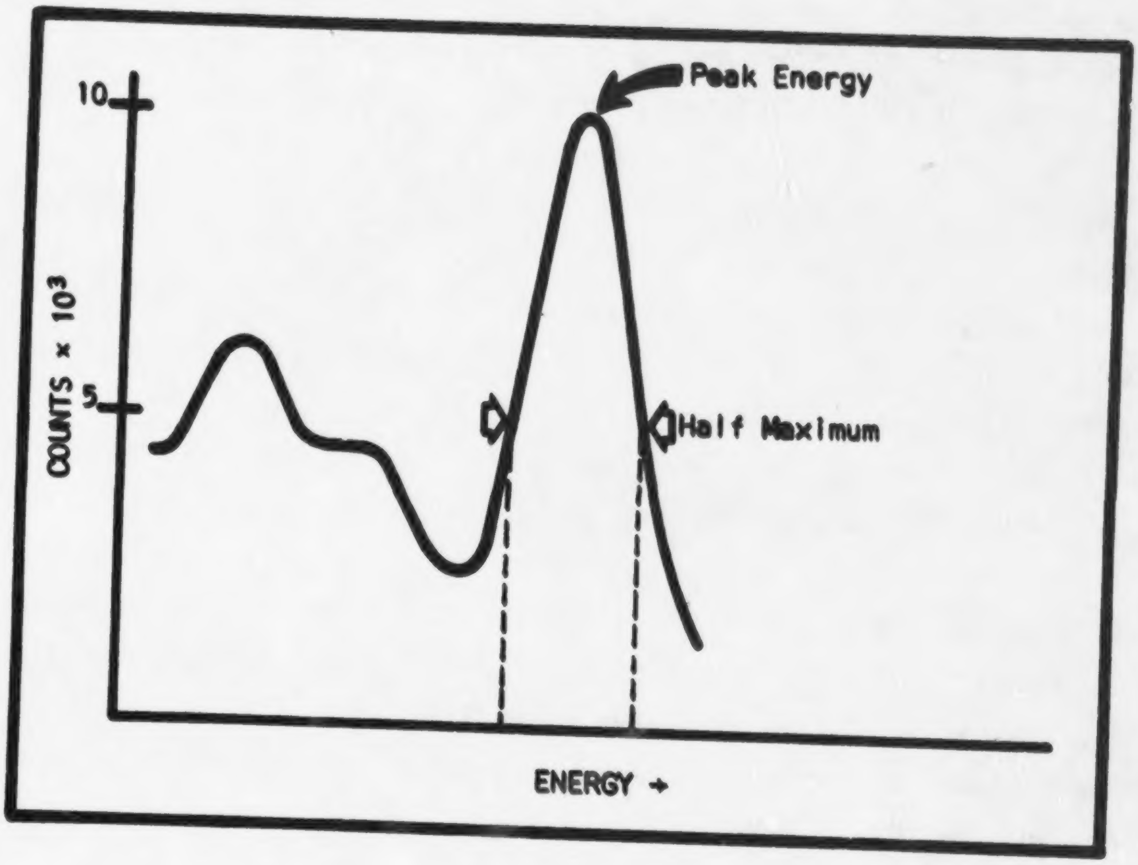


Figure 1.1.3-4 Determination of resolution

purposes of calculation.

$$\text{Resolution (\%)} = \frac{\text{peak width in energy at half maximum count rate}}{\text{peak energy}} \times 100$$

Resolution is a function of energy, and in general it decreases with increasing energy. Cesium 137 has been generally accepted as the standard for comparison of resolution. It is therefore important to specify the energy in reporting resolution when it has been determined at photopeaks other than the 0.662 MeV peak of cesium 137. A typical resolution for a 4-inch by 4-inch NaI(Tl) crystal with a 3-inch phototube is about 8.5 percent for cesium 137.

Linearity

Before any calibration or sample counting can be attempted, the analyzer must be linear. To determine this, a combination of accurately known gamma energies covering a substantial portion of the spectral region of interest must be measured. Gamma energy is then plotted against the channel number at which its photopeak occurs. Zero energy should be at the origin, and a nearly straight line with a slope approximately equal to one should be obtained. If the analyzer is linear, channel number 25 should represent one-fourth the energy represented by channel number 100.

Non-linearity can be corrected by analyzer adjustments described in the manufacturer's instruction manual. Daily checks should be made to ensure that the system remains linear.

Procedures for Interpreting Gamma Spectra

The advent of multichannel pulse height analysis for gamma spectrometry initiated an entirely new method of collecting data. At first, all results were qualitative, but invariably the question arose of how much of each was present. The question was first asked in reference to iodine 131 in milk samples because of the significance of this radionuclide as a potential health hazard.

The first approach to quantitating individual components in a mixture of gamma emitters was to smooth off the bottom of each peak at the Compton continuum, and relate area under that peak, in counts per minute, to the disintegration rate of the nuclide represented. As a refinement of this, spectrum stripping was developed. In this procedure, individual components were graphically separated. Next came the simultaneous equation approach for unscrambling the spectrum, and recently the least squares method and modifications of it have been used. Each of these techniques will be discussed separately.

Before any spectral analysis can be performed, a library of spectra must be obtained for all the radionuclides of interest in all the various sample sizes and shapes. This channel-by-channel spectral information is necessary not only for calibration purposes but also for quantifying the data obtained from radionuclide mixtures.

1. Compton Continuum Subtraction

The easiest way to obtain an estimate of the activity for each radionuclide in a spectrum is to smooth off each photopeak and determine the contribution to that photopeak from the gamma photon occurring at that energy. This method is illustrated in Figure 1.1.3-5.

The difference between the count rate on the dotted line and the count rate at the peak represents the contribution from the gamma photon producing the peak. As an example, channel 18 has 5000 counts and the dotted line passes through the 1000-count portion of the graph. The contribution of this photopeak to channel 18 is 4000 counts. The 1000 counts represents the Compton contribution from gamma photons of higher energy. If the counting efficiency for this radionuclide was determined over five channels, then two channels on each side of the peak must be used to obtain a corrected count rate. The net counts per minute are then divided by the efficiency to obtain the disintegration rate.

This method is satisfactory when the peak is fairly well defined and when no other photopeaks are immediately adjacent and overlapping the peak being quantified. The method only corrects for Compton interference, gamma photons interacting with less than their full energy. At best, the corrected result is an approximation which is quite satisfactory if the photopeak is relatively high compared to the interference. It is not satisfactory, however, if the peak is only slightly above the Compton continuum. The placement of the dotted line involves some subjective judgment, but this is not a serious problem when the same analyst interprets spectra from both standard and sample.

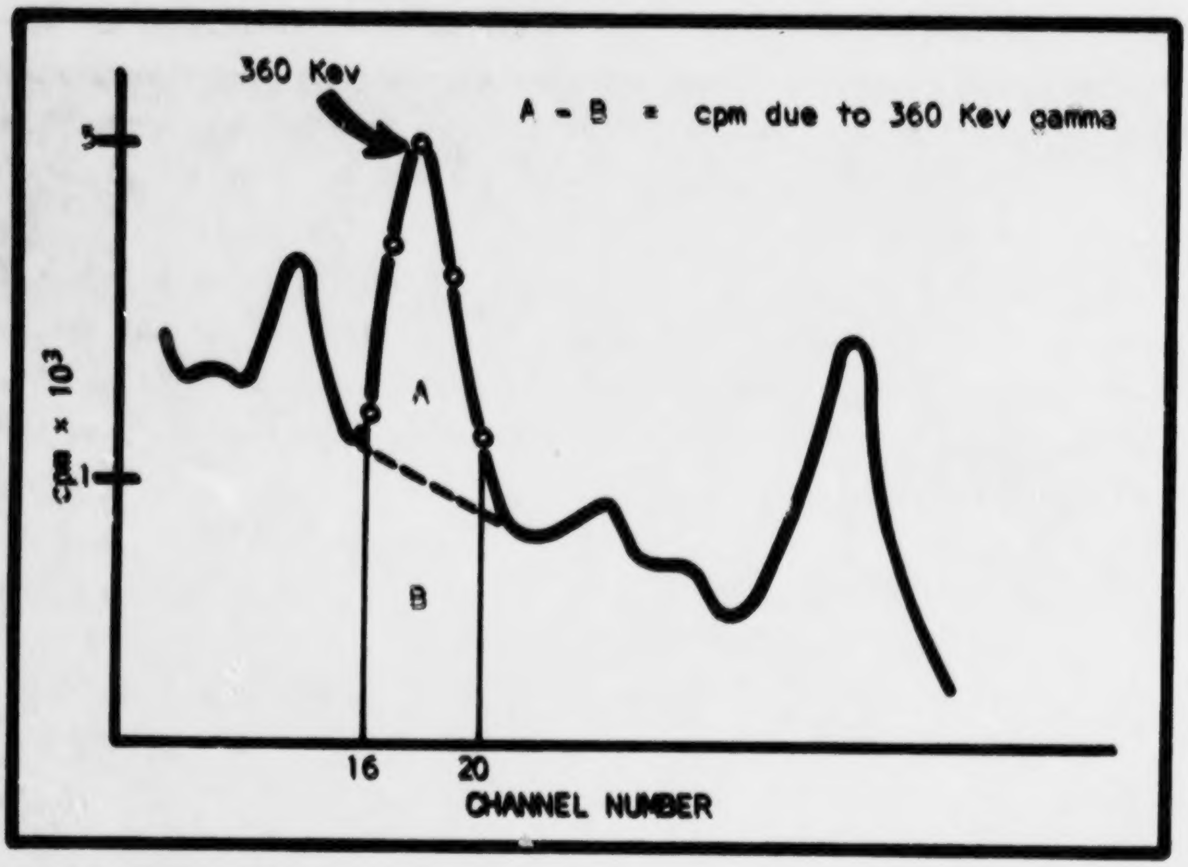


Figure 1.1.3-5 Compton continuum subtraction

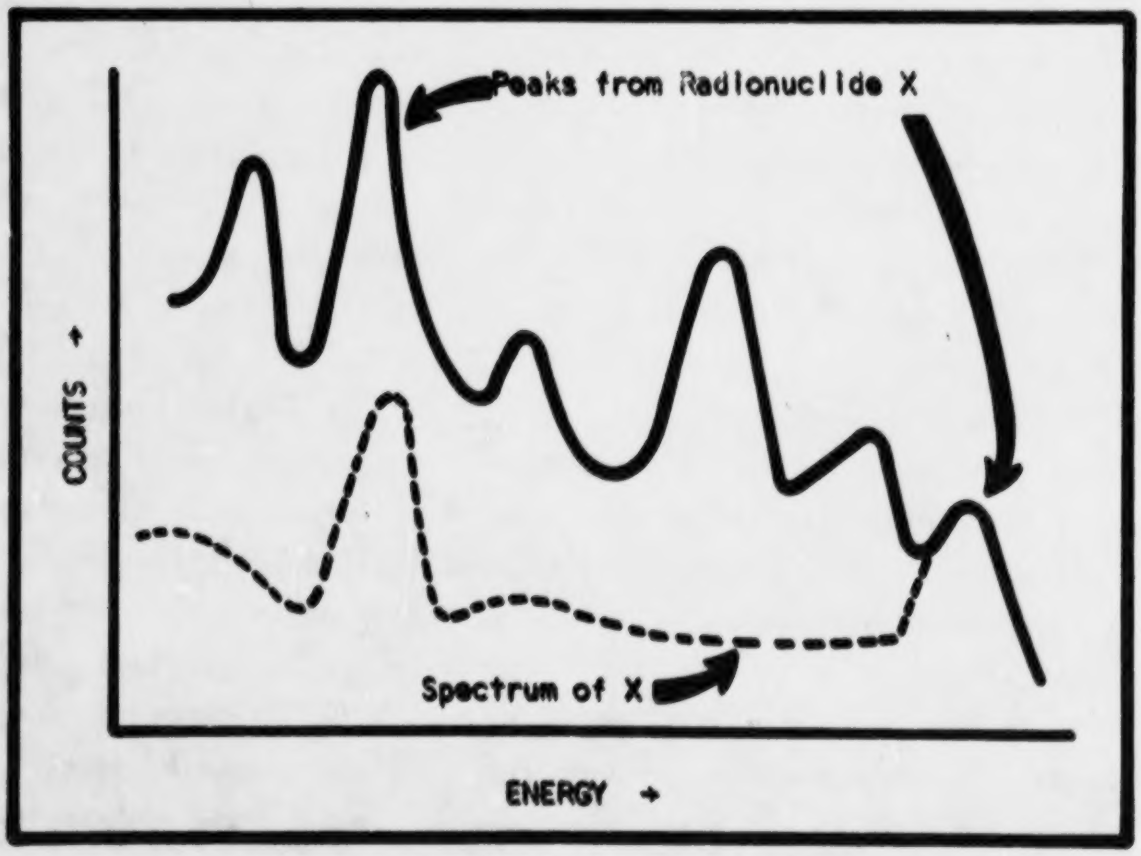


Figure 1.1.3-6 Spectrum stripping

2. Spectrum Stripping

An improvement on Compton continuum subtraction is the spectrum stripping technique. This can be performed by the analyzer, by computer, or graphically by the analyst. Since only some analyzers have this capability, and a computer program is beyond the scope of this discussion, the graphic technique will be described. All three techniques are basically the same except for their mechanics.

Spectrum stripping consists of taking the photopeak of highest energy from a sample spectrum and identifying it with the spectrum of a known radionuclide. The highest energy photopeak of the sample spectrum is superimposed on the peak in the known spectrum. This known spectrum is then subtracted channel by channel from that of the sample to yield a corrected resultant spectrum containing the radionuclides remaining in the sample. The highest energy photopeak in this corrected spectrum is then identified and stripped from the spectrum in the same way. This is continued until all peaks have been identified and an individual spectrum is obtained for each of the radionuclides present in the sample. These individual spectra are used to quantify the data.

For mixtures of few radionuclides, the stripping technique is satisfactory, but each time a spectrum is subtracted a counting error is added to the resultant spectrum. Consequently, at the lower energies the error may be quite significant. An even greater problem exists when the sample contains a radionuclide which emits photons of high energy and low abundance as well as photons having lower energy and high abundance. The spectrum obtained from such a mixture is illustrated in Figure 1.1.3-6. Counting statistics for the high energy peak are poor, and a large error results from stripping out this component.

The problem is intensified when gamma photons of similar energies from two different nuclides form the highest peak in the spectrum. In this situation, spectrum stripping results in an over-subtraction.

In summary, spectrum stripping has application for relatively simple mixtures of radionuclides, but is inadequate for complex spectra. Some persons feel these difficulties can be overcome by using a computer, but this observer knows of no successful program that compares favorably with either the simultaneous equation method or some form of the least squares technique.

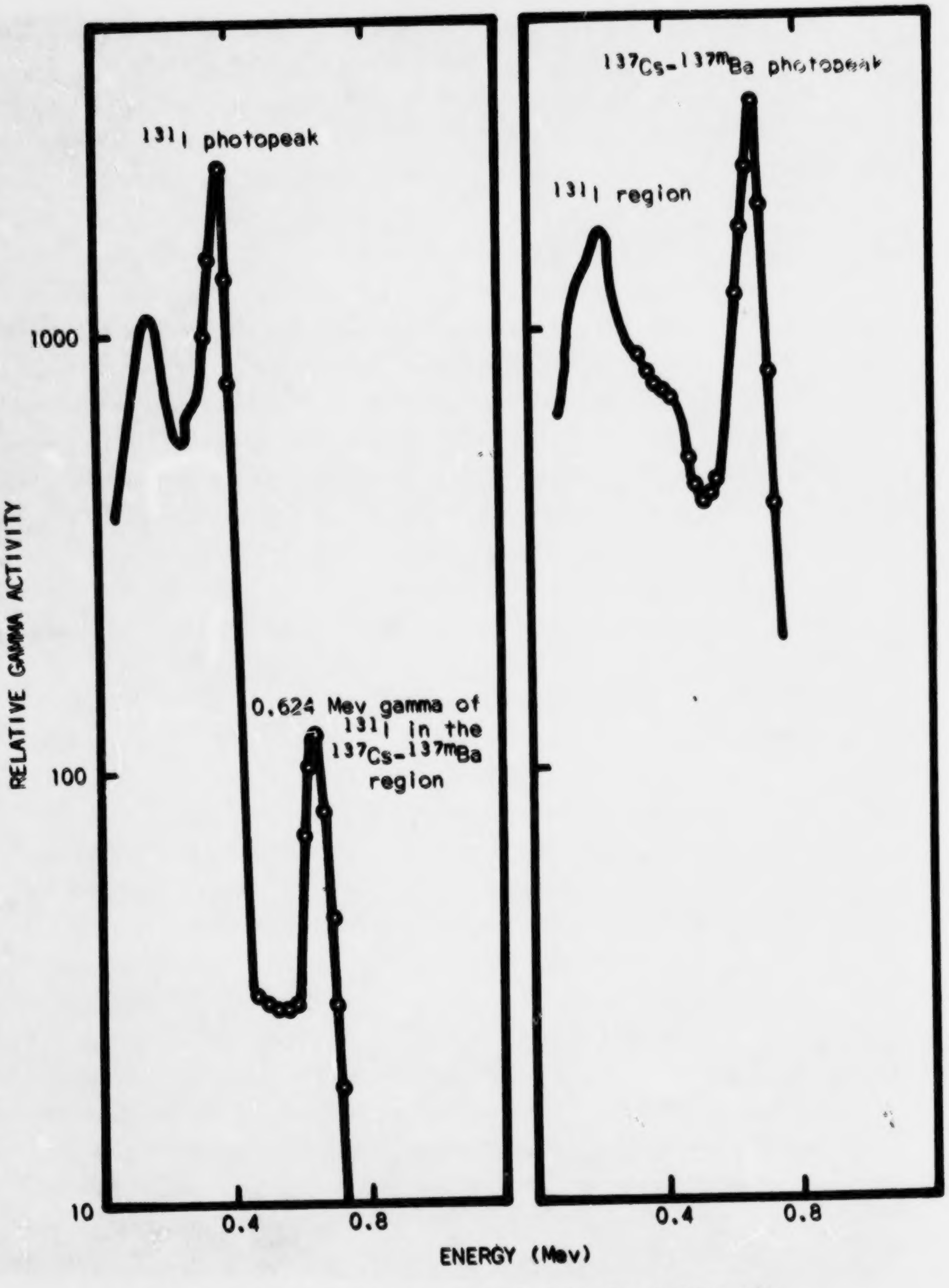


Figure 1.1.3-7 Gamma spectral data for iodine 131 and for cesium 137-barium 137m

3. Simultaneous Equations Method

The simultaneous equations method, commonly called the matrix method, utilizes only the photopeak areas of the sample spectrum. This technique involves solving simultaneous equations to correct for the interference of one radionuclide in the peak of another. A simple two-component sample can best demonstrate the method.

Figure 1.1.3-7 shows an iodine 131 spectrum on which is indicated the photopeak region of iodine 131 and of cesium 137-barium 137m. At the right is a cesium 137 spectrum showing the same regions. These regions are identical with those scanned to determine counting efficiency for each nuclide. The summation of the cesium 137 area on the iodine 131 spectrum simply yields the fraction of the cesium-barium peak area contributed by the 0.624 MeV peak of iodine 131. This fraction is based on the iodine 131 peak as equal to one. The reverse is true for cesium 137 in the iodine 131 peak area.

If we call the iodine 131 nuclide I, and call the cesium 137-barium 137 nuclide C, then it is possible to express the count rate contributed by C to the photopeak of I as a fraction of the count rate contributed by C to the photopeak of C. This is shown mathematically as

$$I_C = F_C C_C$$

where I_C = the count rate contributed to the photopeak of I by C

F_C = the ratio of the count found in the photopeak area of I and contributed by C, to the count contributed to the photopeak of C by C

C_C = the count rate contributed to the photopeak of C by C

This ratio F_C is determined from the individual spectrum of cesium 137, as shown in Figure 1.1.3-7. As an example, if there are 10,000 net counts in the photopeak of the cesium spectrum over the designated channels, and 3,000 net counts in the iodine 131 portion of the spectrum from cesium, there would be an interference factor of cesium in iodine equal to 0.30.

For the mixture of iodine 131 and cesium 137 we obtain the following equations:

$$G_I = B_I + I_I + f_C C_C$$

$$G_C = B_C + C_C + f_I I_I$$

where G_I = gross count rate observed in photopeak of I
G_C = gross count rate observed in photopeak of C
B_I = background count rate in photopeak of I
B_C = background count rate in photopeak of C
I_I = count rate in photopeak of I contributed by I
C_C = count rate in photopeak of C contributed by C
f_I = fractional contribution of I to C
f_C = fractional contribution of C to I

All the above coefficients and count rates except I_I and C_C can be determined from spectral data. Since we have two unknowns and two equations, we use the following determinants:

$$I_I = \frac{\begin{vmatrix} (G_I - B_I) & f_C \\ (G_C - B_C) & 1 \end{vmatrix}}{\begin{vmatrix} 1 & f_C \\ f_I & 1 \end{vmatrix}} \quad \text{and} \quad C_C = \frac{\begin{vmatrix} 1 & (G_I - B_I) \\ f_I & (G_C - B_C) \end{vmatrix}}{\begin{vmatrix} 1 & f_C \\ f_I & 1 \end{vmatrix}}$$

When solved, we obtain

$$I_I = \frac{(G_I - B_I) - f_C(G_C - B_C)}{1 - f_I f_C}$$

and

$$C_C = \frac{(G_C - B_C) - f_I(G_I - B_I)}{1 - f_I f_C}$$

The net counts per minute, corrected for interference, are then divided by the counting efficiency to obtain the disintegration rate for each nuclide.

This matrix method was first developed for determining iodine 131, cesium 137, barium 140, and potassium 40 in 3.5-liter samples of milk.

To expand the two-by-two matrix to fit this situation, four equations for the radionuclides are set up. Assuming that the counts in each channel are net counts, that the background spectrum has been subtracted, we have the following set of equations:

$$N_I = I_I + {}_If_cC_c + {}_If_bB_b + {}_If_kK_k$$

$$N_c = {}_cf_II_I + C_c + {}_cf_bB_b + {}_cf_kK_k$$

$$N_b = {}_bf_II_k + {}_bf_cC_c + B_b + {}_bf_kK_k$$

$$N_k = {}_kf_II_I + {}_kf_cC_c + {}_kf_bB_b + K_k$$

where ${}_If_c$ is the fractional contribution by ^{137}Cs to the photopeak of ^{131}I; I, c, b, and k denote ^{131}I, ^{137}Cs, ^{140}Ba, and ^{40}K, respectively; N_I is the net count rate in the photopeak of ^{131}I, not corrected for interference of other nuclides (cpm); I_I is the count rate contributed by ^{131}I to the photopeak of ^{131}I (cpm), and is the number being solved for; and the remaining terms are self-explanatory.

Before being solved, a typical set of simultaneous equations may appear as follows:

$$\text{net cpm } ^{131}\text{I} = 1.000(I_I) + 0.826(B_b) + 0.339(C_c) + 0.347(K_k)$$

$$\text{net cpm } ^{140}\text{Ba} = 0.018(I_I) + 1.000(B_b) + 0.194(C_c) + 0.229(K_k)$$

$$\text{net cpm } ^{137}\text{Cs} = 0.066(I_I) + 0.248(B_b) + 1.000(C_c) + 0.306(K_k)$$

$$\text{net cpm } ^{40}\text{K} = 0.000(I_I) + 0.125(B_b) + 0.000(C_c) + 1.000(K_k)$$

When solved simultaneously, these equations become:

$$I_I = + 1.027(N_I) - 0.785(N_b) - 0.196(N_c) - 0.117(N_k)$$

$$B_b = - 0.006(N_I) + 1.080(N_b) - 0.207(N_c) - 0.182(N_k)$$

$$C_c = - 0.067(N_I) - 0.174(N_b) + 1.056(N_c) - 0.260(N_k)$$

$$K_k = + 0.000(N_I) - 0.135(N_b) + 0.026(N_c) + 1.102(N_k)$$

The solved values now give the corrected count per minute, or count rate, for each radionuclide. The N_I, N_b, N_c, and N_k, terms in each equation are the net count rate in each photopeak before correction. After the I_I, B_b, C_c, and K_k values are determined, each is divided by the appropriate efficiency to determine the disintegration rate. Once the equations are solved, and the instrument is maintained by quality control charting (see SECTION 2 and 1.3 of this Section) as it was when the individual spectra were obtained, they can be used again and again.

The matrix method requires that all radionuclides in the sample be included, since overlooking one may contribute a large error. For a mixture of four radionuclides, the matrix is not too cumbersome to be solved by hand, but beyond this a simple computer program is recommended. The solved equations can be checked by plugging in the results from the individual calibration spectra used to obtain the efficiency values and interference factors, or by making a mixture of known amounts of standards and obtaining its spectrum.

4. Least-Squares Spectrum Unscrambling

The technique commonly called "least squares" assumes that the count rate in a given channel I is a linear combination of known standard spectra compiled under identical conditions, plus a random error. If we let X_{IJ} be the count rate in channel I due to the presence of the J^{th} library standard nuclide, and let Y_I be the composite count rate for the sample, we have the equation

$$Y_I = \sum_{J=1}^{P} X_{IJ} B_J + r_I$$

where B_J represents the percentage of the J^{th} library standard contributing to the composite sample spectrum, and r_I the random error in channel I.

By minimizing the sum of the squares of the residuals by least-squares techniques, we obtain a set of matrix equations which can be solved for the B components.

By using data from all channels of the spectrometer, this procedure considers more information than do techniques, such as the matrix method, where part of the spectrum is essentially discarded.

The least-squares method is therefore best to use on very complex gamma spectra. Error calculations are inherent in the method, and statistical tests can be applied to determine the precision and degree of significance of the results.

With these advantages, the least-squares method has the disadvantage of being very unreliable when stringent conditions of stability are not imposed upon the radiation detection equipment. A slight instrument or photomultiplier drift becomes intolerable when the least-squares method is applied. A computer is also essential to unscramble complex gamma spectra by this technique of solving simultaneous equations. Because the computer program must be designed for the available equipment, no attempt will be made to describe a typical program here.

1.2 CALCULATION OF RESULTS AND COUNTING ERROR

1.2.1 Integral Counting

Any of the integral counters provide a gross count rate which consists of counts due to both sample and background activity. To determine the activity from the sample alone, the background count rate of the instrument with no sample present, but otherwise identical, must be obtained. A clean sample container, similar to that used for the sample, should be in place for the background determination. The background count rate is subtracted from the sample count rate to obtain a net counting rate. This net count rate is then divided by the counting efficiency, previously determined for the particular sample type, to obtain the disintegration rate of the sample. The following equation expresses this relationship.

$$\text{Disintegration Rate (dpm)} = \frac{\text{Gross Count Rate (cpm) - Background Count Rate (cpm)}}{\text{Efficiency (cpm/dpm)}}$$

To express the result in activity units of picocuries per liter (or per gram, etc.), the equation becomes:

$$\text{Activity (pCi/liter)} = \frac{\text{Gross Count Rate (cpm) - Background Count Rate (cpm)}}{\text{Efficiency (cpm/dpm)} \times 2.22\ \text{dpm/pCi} \times \text{Sample Volume (liters)}}$$

A large enough sample must be taken to insure that the disintegration rate will be statistically significant and not primarily the result of counting error. This counting error can be determined as follows:

$$E = Z\left(\frac{S}{t_s} + \frac{B}{t_b}\right)^{\frac{1}{2}}$$

where E = permissible counting error (cpm)

Z = the constant associated with a given confidence level

S = gross count rate of the sample (cpm)

B = background count rate (cpm)

t_s = duration of sample count, or sample counting time (minutes)

t_b = duration of background count, or background counting time (minutes)

As an example, assume the gross count rate of the sample to be 120 counts per minute and the background count rate to be 40 counts per minute. If the counting time of the sample is 30 minutes, and the counting time of the background is 100 minutes, the counting error at the 95 percent confidence level will be

$$\begin{aligned} E &= \pm 1.96 \left(\frac{120}{30} + \frac{40}{100} \right)^{\frac{1}{2}} \\ &= \pm 1.96 \left(4 + 0.4 \right)^{\frac{1}{2}} \\ &= \pm 4.2 \text{ cpm} \end{aligned}$$

The sample then has a net count rate of 80 ± 4.2 counts per minute, or slightly more than a 5 percent counting error at the 95 percent confidence level. This means that we are 95 percent certain that the true count rate for the sample lies between 75.8 and 84.2 counts per minute.

When the conversion is made from counts to disintegrations, care must be taken to obtain the proper efficiency value. For alpha or beta counting, self-absorption in the sample can be very significant, and appropriate efficiency values must be determined and applied. For particle counting, either alpha or beta, backscatter from the sample container contributes to the count rate, and the efficiency values must be obtained for the proper container, which is the same container in which the samples will be counted.

1.2.2 Spectral Analysis

As described earlier, there are several ways to determine the counting rate for each gamma-emitting radionuclide in a gamma spectrum. (See "Procedures for Interpreting Gamma Spectra" under GAMMA SPECTROMETER in part 1.1.3 for methods of calculation.) By various techniques, one obtains a net count rate which is then corrected to a disintegration rate by dividing by the appropriate counting efficiency.

It should be noted that the counting error for each radionuclide in a complex spectrum is difficult to determine mathematically, and that the method used for integral counting does not apply. There are errors associated with each radionuclide in its own and other photopeak areas. In general, the more radionuclides present in the spectrum the larger the error becomes for any single nuclide, but the percentage of interference is of primary importance. It should also be noted that low-energy gamma photons do not add to the counting error of high-energy gamma photons.

1.3 RADIOACTIVE STANDARDS

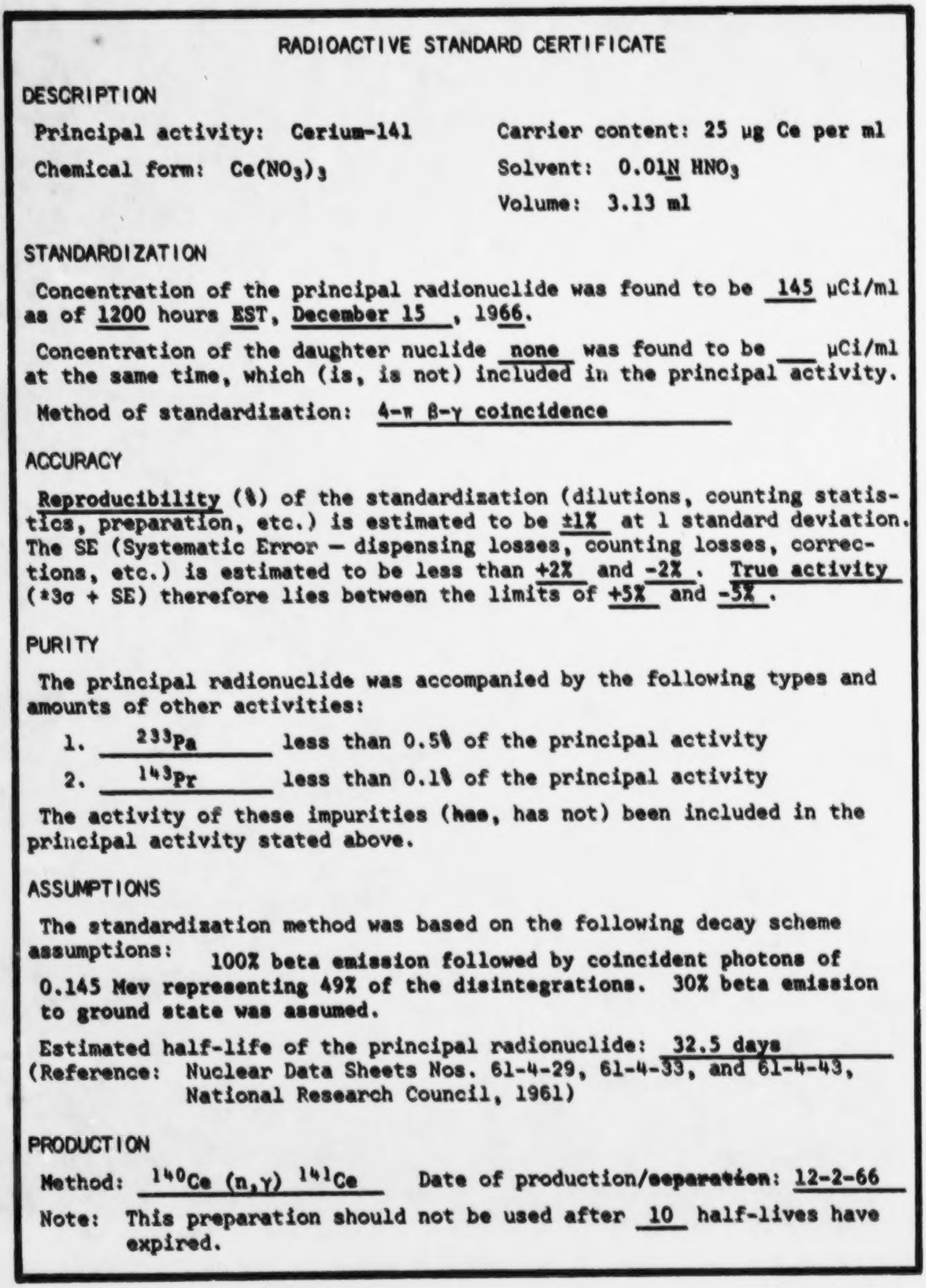
1.3.1 Description of Available Standards

The proper selection and proper use of standards for calibrating any detection system are both essential to obtain reliable quantitative results. Many suppliers provide under the name of "standards" nothing more than poorly rated sources. There have been many instances where the rating of these "standards" deviated from the true activity rating by more than a factor of two. The only excusable errors are those resulting from poorly known decay schemes and half-lives, and from difficult chemical separations.

Several suppliers use a secondary means of standardization based on a poor primary standard. Error terms given with most of the standards are almost meaningless because they are not defined. As an example, a "standard" might be rated "1.1×10^5 disintegrations per second ±10%". Is this "±10%" a counting error, and if so, at what confidence interval is it determined? Does it include systematic error, and what assumptions have been made?

The decay scheme used in standardization should be identified by the supplier, since there are discrepancies in reported decay schemes for most nuclides, and for some methods of standardization a knowledge of the decay scheme is essential. The amount and the chemical form of carrier added to the standard can also be of importance in minimizing adsorption on the container walls or volatilization of the solution. Such information is needed to make accurate dilutions for calibrating, since most standards have too high a disintegration rate to be counted on sensitive laboratory instruments without prior dilution. A model certificate is included as Figure 1.3.1-1 to demonstrate the information desired on a radioactive standard certificate.

It is essential that any standard prepared for instrument calibration be counted in the same geometrical configuration as the samples. Thus, if a 3.5-liter milk sample is to be counted, the counting system must be calibrated for that volume in an identical container for each radionuclide of interest.



RADIOACTIVE STANDARD CERTIFICATE

DESCRIPTION

Principal activity: Cerium-141

Chemical form: $Ce(NO_3)_3$

Carrier content: 25 µg Ce per ml

Solvent: 0.01N HNO_3

Volume: 3.13 ml

STANDARDIZATION

Concentration of the principal radionuclide was found to be 145 µCi/ml as of 1200 hours EST, December 15, 1966.

Concentration of the daughter nuclide none was found to be ___ µCi/ml at the same time, which (is, is not) included in the principal activity.

Method of standardization: 4-π β-γ coincidence

ACCURACY

Reproducibility (%) of the standardization (dilutions, counting statistics, preparation, etc.) is estimated to be ±1% at 1 standard deviation. The SE (Systematic Error — dispensing losses, counting losses, corrections, etc.) is estimated to be less than +2% and -2%. True activity ($\pm 3\sigma$ + SE) therefore lies between the limits of +5% and -5%.

PURITY

The principal radionuclide was accompanied by the following types and amounts of other activities:

1. ^{233}Pa less than 0.5% of the principal activity
2. ^{143}Pr less than 0.1% of the principal activity

The activity of these impurities (~~has~~, has not) been included in the principal activity stated above.

ASSUMPTIONS

The standardization method was based on the following decay scheme assumptions: 100% beta emission followed by coincident photons of 0.145 Mev representing 49% of the disintegrations. 30% beta emission to ground state was assumed.

Estimated half-life of the principal radionuclide: 32.5 days
(Reference: Nuclear Data Sheets Nos. 61-4-29, 61-4-33, and 61-4-43, National Research Council, 1961)

PRODUCTION

Method: $^{140}Ce\ (n,\gamma)\ ^{141}Ce$ Date of production/~~separation~~: 12-2-66

Note: This preparation should not be used after 10 half-lives have expired.

Figure 1.3.1-1 A proposed certificate for a radioactivity standard

The standards described here are liquid, since solutions are most conveniently used to simulate samples. This is not to minimize the usefulness of solid performance and linearity sources used on a daily basis. These, however, need not be absolute standards but merely relative standards for daily checking of the instruments after absolute standardization has been performed. Performance standards are further discussed under 1.4.1.

A partial list of the suppliers of standards is included with a brief statement or quotation to indicate how well their standards are rated. Do not be misled by the smaller error terms listed by some suppliers. The Radiochemical Center in Amersham, England follows the model certificate very closely, whereas some others give only the barest essentials.

1. RCC — Radiochemical Center, Amersham, England
   Accuracy statements consider random and systematic errors, and range from 0.5 to 5% at one standard deviation.

2. NBS — National Bureau of Standards, Washington, D. C.
   Accuracy generally stated to be within "±1%" or "±2%".

3. IAEA — International Atomic Energy Agency, Vienna, Austria
   Accuracy generally given as "±1%".

4. AL — Abbott Laboratories, Oak Ridge, Tennessee
   "Values are accurate to ±5%."

5. IS — Iso/Serve, Incorporated, Cambridge, Massachusetts
   "5% standard solutions"

6. NC — Nuclear-Chicago Corporation, Des Plaines, Illinois
   "Stated activity within ±3% of true value."

7. NCA — Nucleonic Corporation of America, Brooklyn, New York
   "Activities accurate to within ±3% of the indicated values.'

8. NENC — New England Nuclear Corporation, Boston, Massachusetts
"Calibration is ±10%."

9. NSEC — Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania
Stated accuracy may be ±2%, ±3%, or ±5%, depending upon the nuclide.

10. TL — Tracerlab, Waltham, Massachusetts
"Stated activity is within ±5% of absolute value."

11. USN — U. S. Nuclear Corporation, Burbank, California
"Accuracy is within ±5%."

1.3.2 Preparation of Standard Solutions

DILUTION

It is invariably necessary to dilute the standard solution as purchased to obtain a source with a convenient disintegration rate for counting. It is common to make dilutions using micropipettes (lambda pipettes). Practice with these pipettes is essential before using them to make accurate dilutions. Care must be taken to wipe the outside of the pipette free of solution before making the transfer. Both the "to contain" and the "to deliver" micropipettes are available. The "to contain" type must be rinsed several times to transfer all the solution originally present in the pipette. The "to deliver" type should not be rinsed, but the last drop should be touched to the side of the container receiving the transfer. Pipettes must be clean and dry for accurate calibration work. Such details are very important, but unfortunately are frequently overlooked.

For convenience and accuracy, a 100-lambda portion of the original solution may be diluted to 10 milliliters in a flask calibrated for that volume. The dilution will be 1-to-100, since 1 lambda is equal to 0.001 milliliter. Pipettes measuring less than 10 lambda should not ordinarily be used, since they are difficult to use with accuracy.

CHEMICAL PROPERTIES OF THE DILUTION

The dilution of the standard should be made using a solution chemically similar to that of the standard. It is not necessary to keep it in the same chemical form, but is usually a good idea. If it is basic or acid, it should remain so unless there is a good reason for changing it and it is known that the pH change will result in no losses due to plating on the walls of the container, precipitation, settling, or volatilization of the radionuclide.

Table 1.3.2-1 shows the chemical form in which some radioactive standards are commonly supplied.

Table 1.3.2-1 Chemical form of some radioactive standard solutions

RADIONUCLIDE	COMPOUND	SOLUTION
^{32}P	H_3PO_4	$1\underline{N}$ HCl ± 50%
^{65}Zn	$ZnCl_2$	$6\underline{N}$ HCl
^{76}As	$HAsO_2$	$1\underline{N}$ HCl ± 50%
^{82}Br	KBr	H_2O
^{90}Sr	$SrCl_2$	$0.1\underline{N}$ HCl
^{95}Zr-^{95}Nb	oxalate complex	~5% oxalic acid
^{99}Tc	NH_4TcO_4	$1\underline{N}$ NH_4OH ± 50%
^{106}Ru	$RuCl_3$	$0.1\underline{N}$ HCl ± $0.2\underline{N}$ HNO_3 per gram of solution
^{122}Sb	$SbCl_3$ + SbOCl	$>6\underline{N}$ HCl
^{131}I	NaI	Na_2SO_3 - NaOH
^{144}Ce	$Ce(NO_3)_3$	$0.01\underline{N}$ HNO_3
^{192}Ir	Na_2IrCl_6	$<0.1\underline{N}$ HCl
^{210}Bi	$Bi(NO_3)_3$	$4\text{-}6\underline{N}$ HNO_3

STORAGE OF STANDARDS

It is important to store the standards in nearly full, tightly sealed containers. If a relatively small volume is kept in a large container, evaporation of the solution takes place, and the concentration of the standard is increased. Thin polyethylene or similar material is not recommended because of transpiration through the walls. Even with these precautions it is advisable to check the standard before further calibration work if several weeks have elapsed since it was last used.

1.4 REQUIREMENTS FOR INSTRUMENT PERFORMANCE

The application of suitable performance checks to the counting laboratory minimizes day-to-day operational variability and preserves the capability of obtaining consistent, reproducible measurements. This constancy is essential for reliable intercomparison of sample counting data, particularly the results of long-term studies. The maintenance of such controls is mandatory for validating results when several laboratories are involved in large-scale surveillance programs or in the analysis of split samples.

The analytical quality control procedures discussed in SECTION 2 apply to the counting as well as to the chemistry laboratory. The sole objective of any counting laboratory's quality control program is the attainment of a level of accuracy consistent with analytical requirements. This goal is achieved by 1) the minimization of systematic error, which is the bias inherent chiefly in the determination of calibration values, data reduction constants, and correction factors, and 2) the improvement of analytical precision which is principally attributable to variations in instrument performance and background fluctuations. Control of the latter becomes important for obtaining maximum sensitivity in measurement of comparatively low-level radioactivities.

1.4.1 Performance Standards

The most important facet of an operational quality control program is the frequent daily testing of instrument performance. This is accomplished by means of a radioactive source which provides a live check of the response of an entire counting system. Such a source is called a performance standard.

The radionuclide chosen as a performance standard should be of long half-life to minimize decay corrections, should be chemically stable, and should be similar in size and energy to the samples being counted. It should be preserved intact by a cover durable enough to prevent losses through handling. A separate standard should be provided for each counting system.

A suitable performance standard for low-background beta counters is strontium 90-yttrium 90 prepared on the planchet commonly used for routine measurements. Another suitable performance standard is cesium 137. These provide satisfactory performance standards for most end-window beta counters unless beta emitters of much lower energy are routinely counted. They are often recommended as calibration standards also, since their $E_{\beta_{max}}$ values simulate the $E_{\beta_{max}}$ of mixed fission products.

Uranium oxide (U_3O_8) is a commonly-employed performance standard for internal proportional counters. For use as a beta standard, it should be covered with heavy-duty aluminum foil, and for use as an alpha source, it should be left uncovered. The U_3O_8 has a wide range of energies which make it suitable as a performance standard for counters which are used routinely to measure the gross count rate of beta-emitter mixtures.

For gamma spectrometry, cesium 137 is recommended as a performance standard. An energy band of about 0.2 MeV is used to obtain the counting rate. The same cesium source should be used to determine resolution at regular intervals. Any deterioration of resolution should be promptly investigated.

The average counting rate of any performance standard is determined by taking at least twenty consecutive measurements on the instrument with which it is to be used. A two or three standard deviation error calculated from the observations defines the tolerance levels for subsequent tests. The activity level of the standard should be sufficient to provide a total count with an error of less than ±1 percent at the 95 percent confidence level for a counting interval of several minutes, but should not be so high that the deadtime is appreciable. Test results exceeding the calculated tolerance levels indicate unacceptable instrument response. The control settings, connectors, or other obvious aspects of the system should be examined for malfunction. If an unacceptable result is duplicated, the instrument is not functioning properly and should be removed from service until repaired.

The common control chart, consisting of graphic plots of tolerance levels and individual results, has been found to be a useful means of readily judging quality of response, that is, whether the variations are purely statistical in nature or are indicative of malfunction. A detailed description of these charts and their application is given in SECTION 2. QUALITY CONTROL. Since these charts can provide a compact history of counting instrument behavior, faulty operation can often be anticipated or diagnosed, and in addition, the data can serve as a basis for reducing tolerances and thereby improve precision.

1.4.2 Background Control

The variations of instrument background are attributable not only to daily and seasonal fluctuation of natural and artificially produced radionuclides in the environment, but also to detector contamination and to the interference of sources inadvertently introduced nearby. Abnormal variations, if allowed, affect analytical precision and lessen the sensitivity for performing relatively low-level assays. The background response of each system must therefore be measured frequently to assure that the natural levels are within the expected range, and to monitor for undesirable sources in the vicinity, especially when counting low-level activities.

There are three criteria for determining the required frequency and duration for these measurements. They are: the range of fluctuation typically experienced; the requirements for analytical precision, bias, and sensitivity; and the likelihood of detector contamination from samples.

A reasonably satisfactory estimate of a system's normal background fluctuation can be obtained by making twenty successive observations of equal duration. Control charts can be adapted to use for determining the occurrence of significant deviations from normal ranges.

Background determinations should be made whenever samples are not being counted. It is important to take measurements at various times of the day to observe whether or not background varies with time of day. This is especially important where radon and thoron daughters are not under control and, therefore, fluctuate throughout the day. False background readings would be observed if background counts were taken during one part of the day and sample counts during another. Once it has been established that the background does not vary during the day, the background count can be taken at any convenient time.

1.4.3 Preventive Maintenance

As a supplement to use of performance standards, frequent measurement of resolution, and adequate control of background, a preventive maintenance program based on the manufacturer's recommendations given in manuals accompanying the instruments should be regularly followed. Such a program anticipates and minimizes deviations from acceptable operating conditions.

On some instruments there are test modes of operation, such as a 60-cycle pulse on scalers, designed to check the electronics. Other systems provide for checks of voltage and pulse shape to insure satisfactory operation. Usually these are early warning techniques which can be utilized to prevent more serious trouble.

1.5 COUNTING ROOM LOCATION AND DESIGN

The low-level radiation counting laboratory should be located away from other laboratories or rooms where tracer levels of activity are present. Natural shielding, such as that in basements, should be utilized wherever possible to reduce the background.

The counting room should be maintained under positive pressure by bringing in from low-radioactivity areas air which has been passed through a high efficiency filtering system, and the laboratory air conditioner should filter the air on a recirculating basis. This air conditioner should be able to maintain a constant temperature and a relative humidity of approximately 60 percent. In addition, the laboratory should be vacuumed regularly to minimize problems from dust which could cause high or spurious background measurements.

Traffic into the counting room should be discouraged. The use of an "IN" and "OUT" box, either as a pass through the wall or in a designated area directly inside the door, will help. The boxes also keep the samples at one location away from the counters, reducing the chance that a sample of high activity will influence the background response of the counters. Because a large number of low-activity samples can collectively constitute a high-activity source, samples must not be stored in the counting room, but should be returned to the originator soon after they are counted.

1.6 CATALOG OF SELECTED GAMMA SPECTRA

Several catalogs of gamma-ray spectra have been compiled and are available in the published literature(6,7). However, with the exception of the catalog compiled by the Division of Radiological Health for trainees attending their Environmental Radiological Health training courses, these do not provide spectra for geometries simulating environmental samples.

The spectra presented in the following pages are primarily for 450-milliliter aqueous samples in 1-pint plastic "cottage cheese" containers (CCC), as shown in Figure 1.1.3-2. The samples were counted directly on the crystal. The detector consisted of a 4-inch by 4-inch cylindrical thallium-activated sodium iodide crystal contained in a can of 0.019-inch thick stainless steel. A mu-metal shield surrounded the 3-inch diameter phototube to minimize the effect of magnetic fields. The resolution obtained was 8.5 percent for a point source of cesium 137 (0.662 MeV).

The detector was surrounded by a steel shield 6 inches thick with interior dimensions of 18 by 18 by 24 inches. No liners were in the shield, so backscatter was somewhat higher than would be obtained with a lined shield.

Spectral data were accumulated on a 200-channel transistorized pulse height analyzer operated at 20 kiloelectron volts per channel. All spectra were plotted by hand from data read out on a typewriter. Some slight peak shifts may be noted on the graphs.

Spectra for both 40 milliliters and 450 milliliters of water containing the same amount of activity were included for cesium 137 and cobalt 60 to show the change in the Compton region for different sample sizes. In addition, a bremsstrahlung spectrum from strontium 90-yttrium 90 is shown to illustrate the effect of beta rays present in the sample.

Spectra included in the previously compiled catalog for trainees were collected in the first 100 channels of a transistorized 400-channel analyzer coupled to a 3-inch by 3-inch crystal. Samples from which these spectra were taken were 3.5-liter solutions in the Marinelli aluminum beakers, also shown in Figure 1.1.3-2. Together the two catalogs should provide a useful reference for gamma spectral analysis of environmental samples.

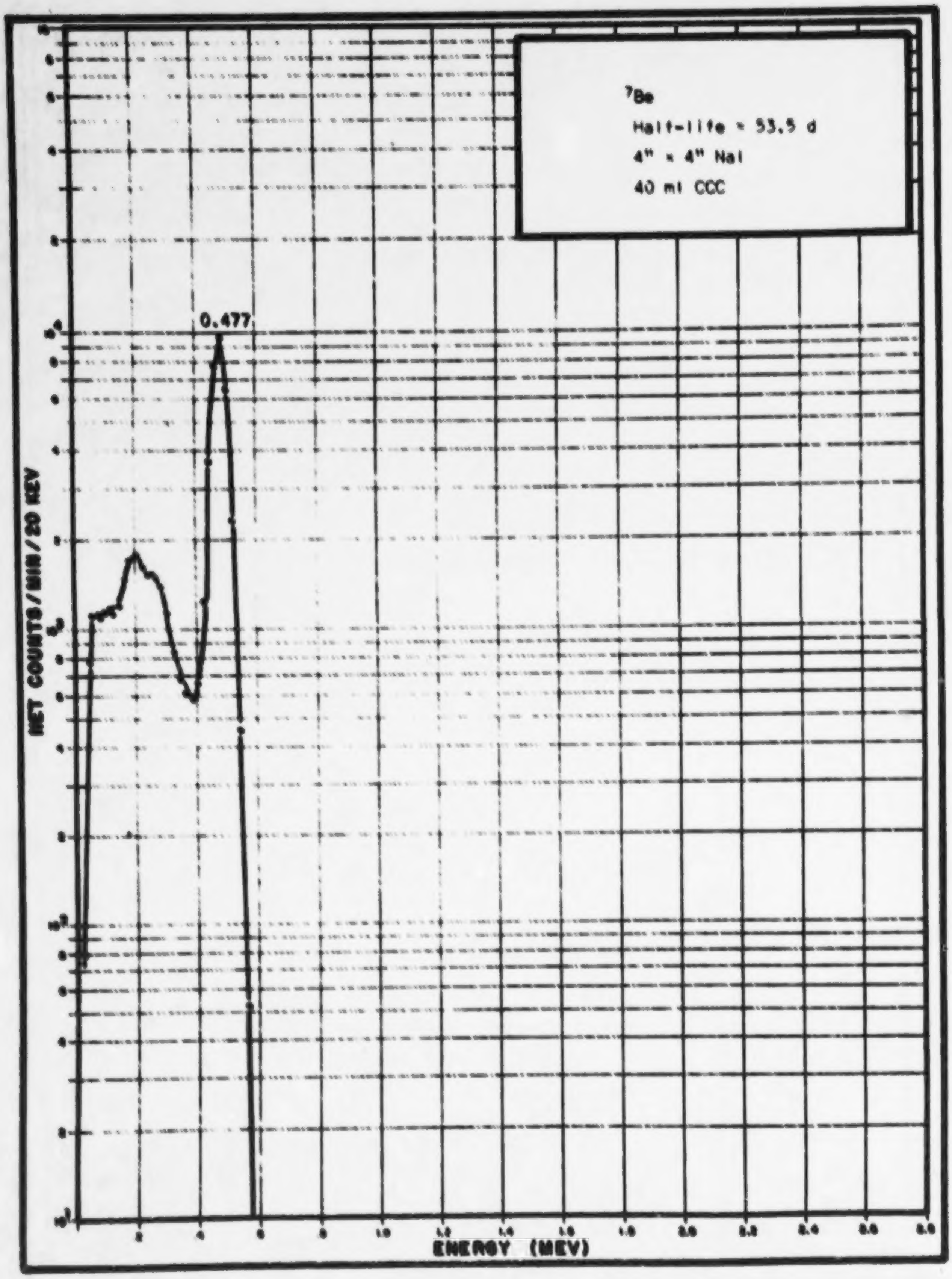


Figure 1.6-1 Gamma spectrum of ^{7}Be - 40 ml

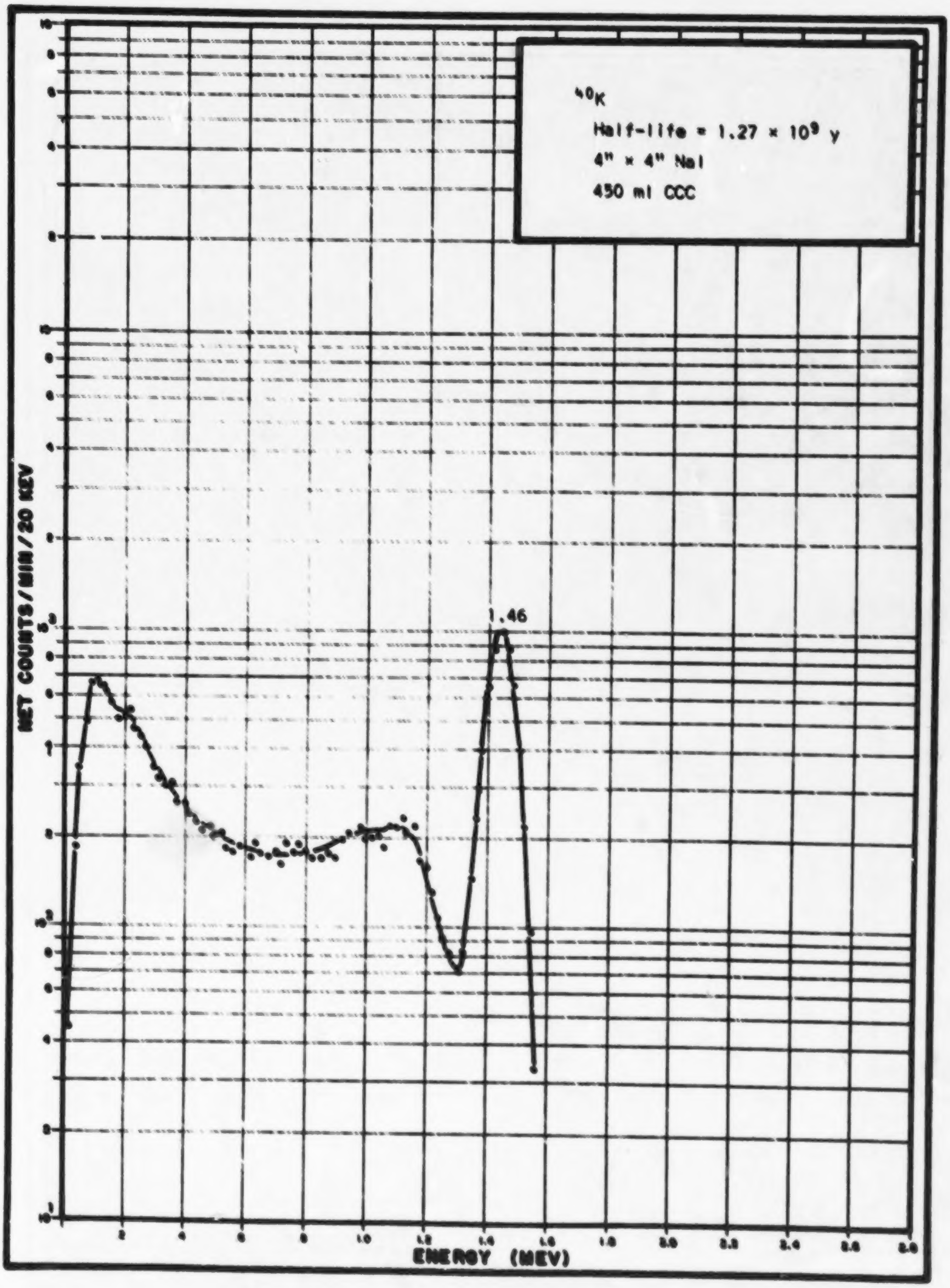


Figure 1.6-2 Gamma spectrum of ^{40}K - 450 ml

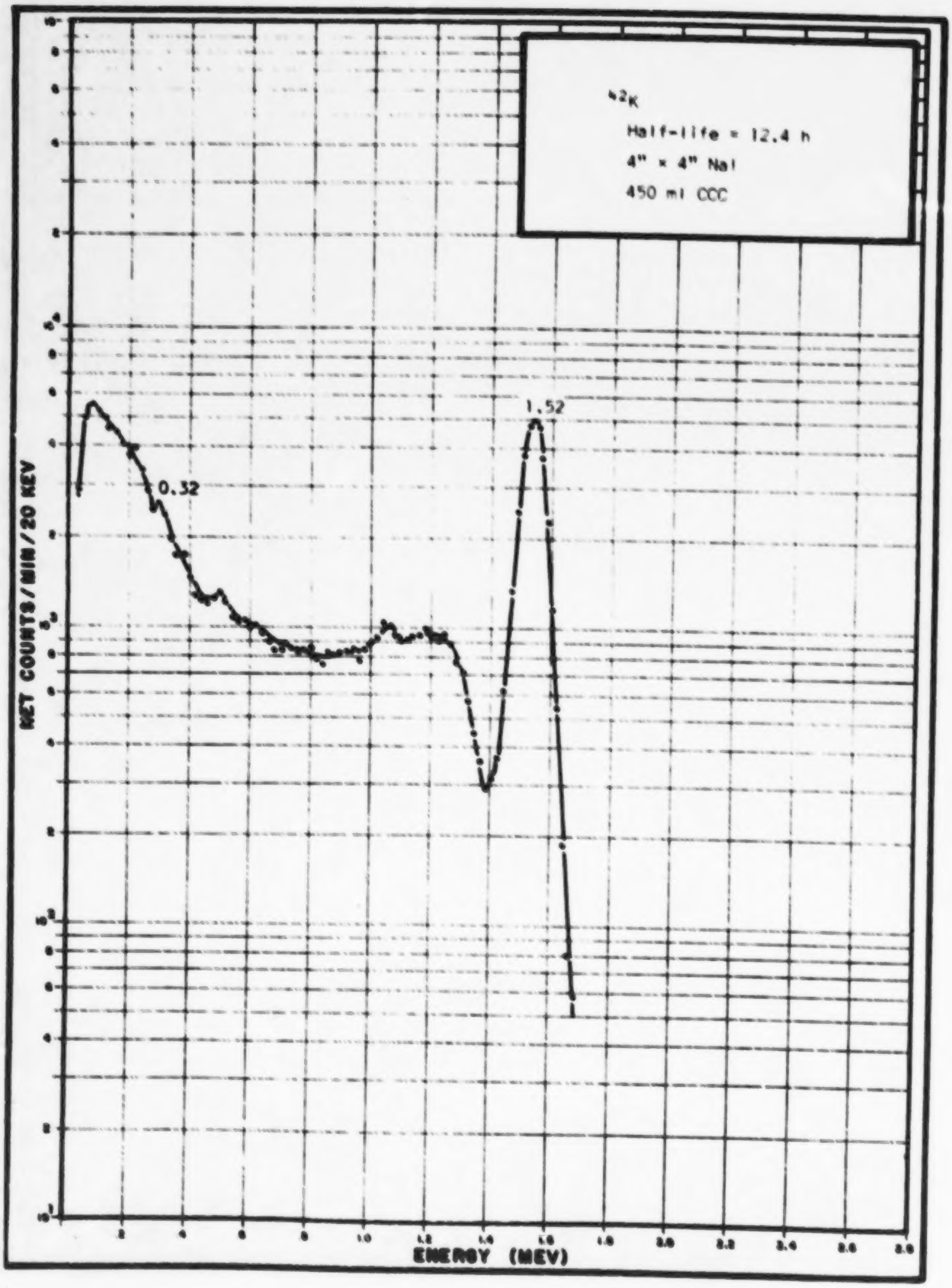


Figure 1.6-3 Gamma spectrum of ^{42}K - 450 ml

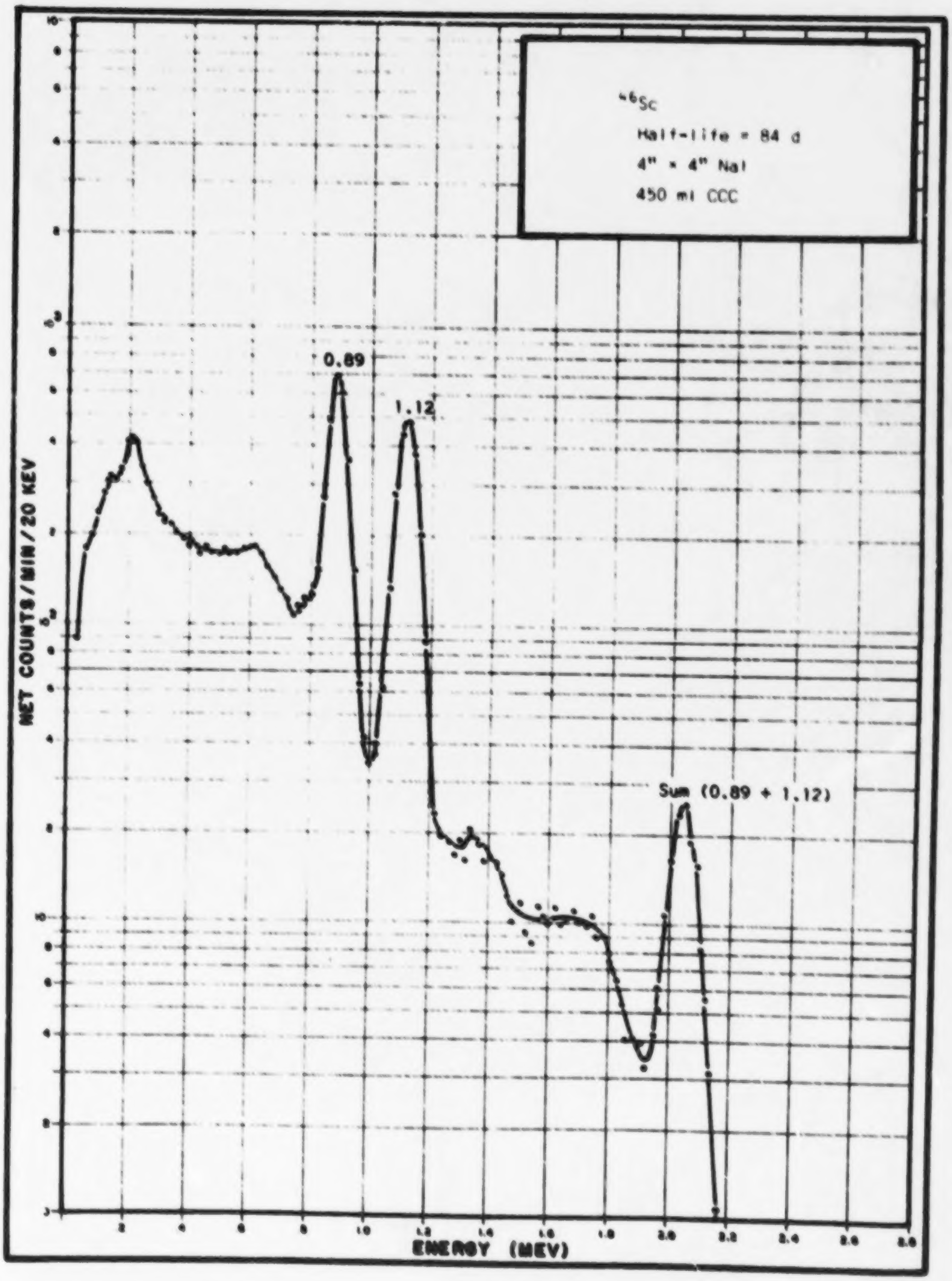


Figure 1.6-4 Gamma spectrum of ^{46}Sc - 450 ml

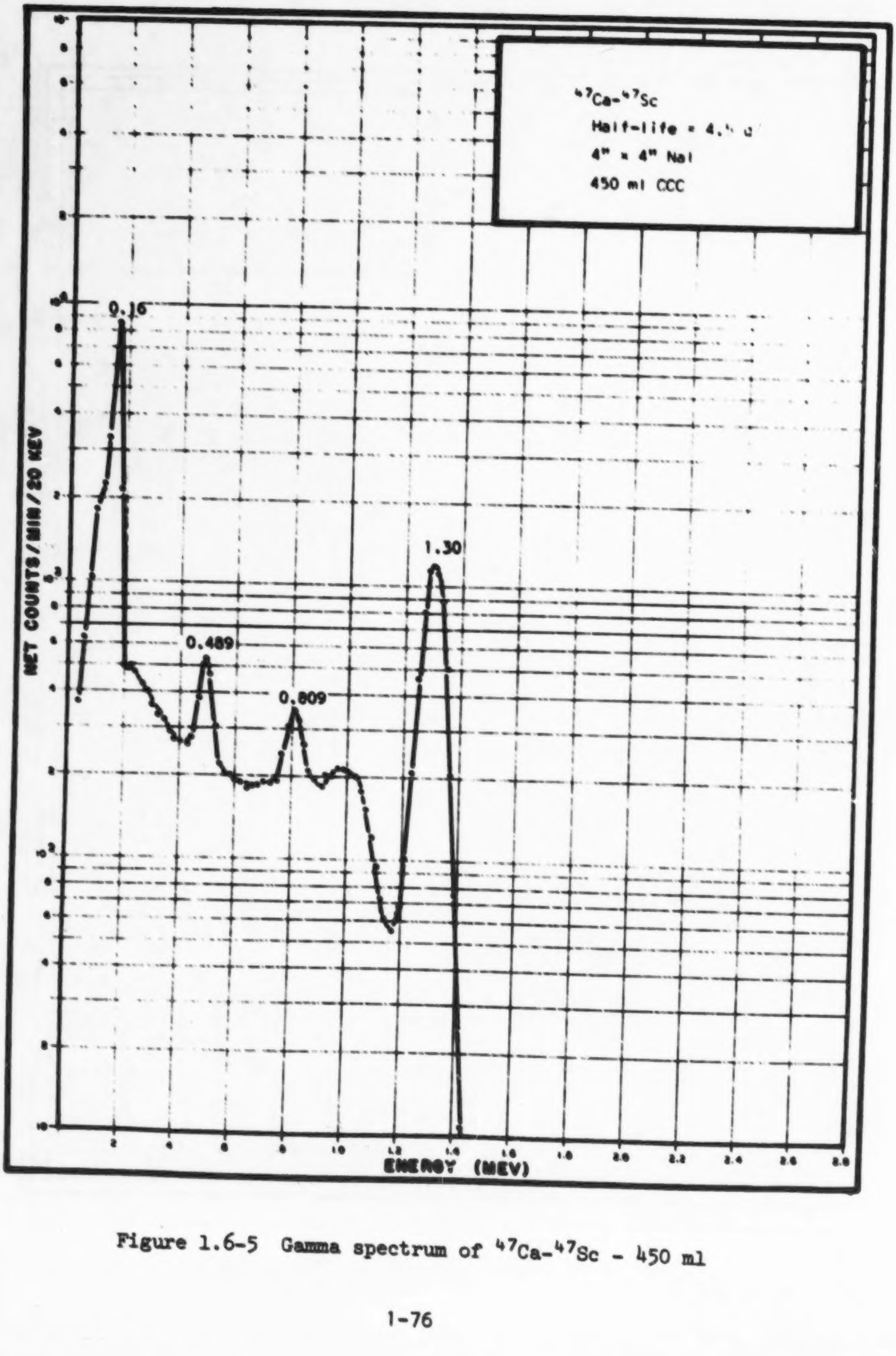


Figure 1.6-5 Gamma spectrum of ^{47}Ca-^{47}Sc - 450 ml

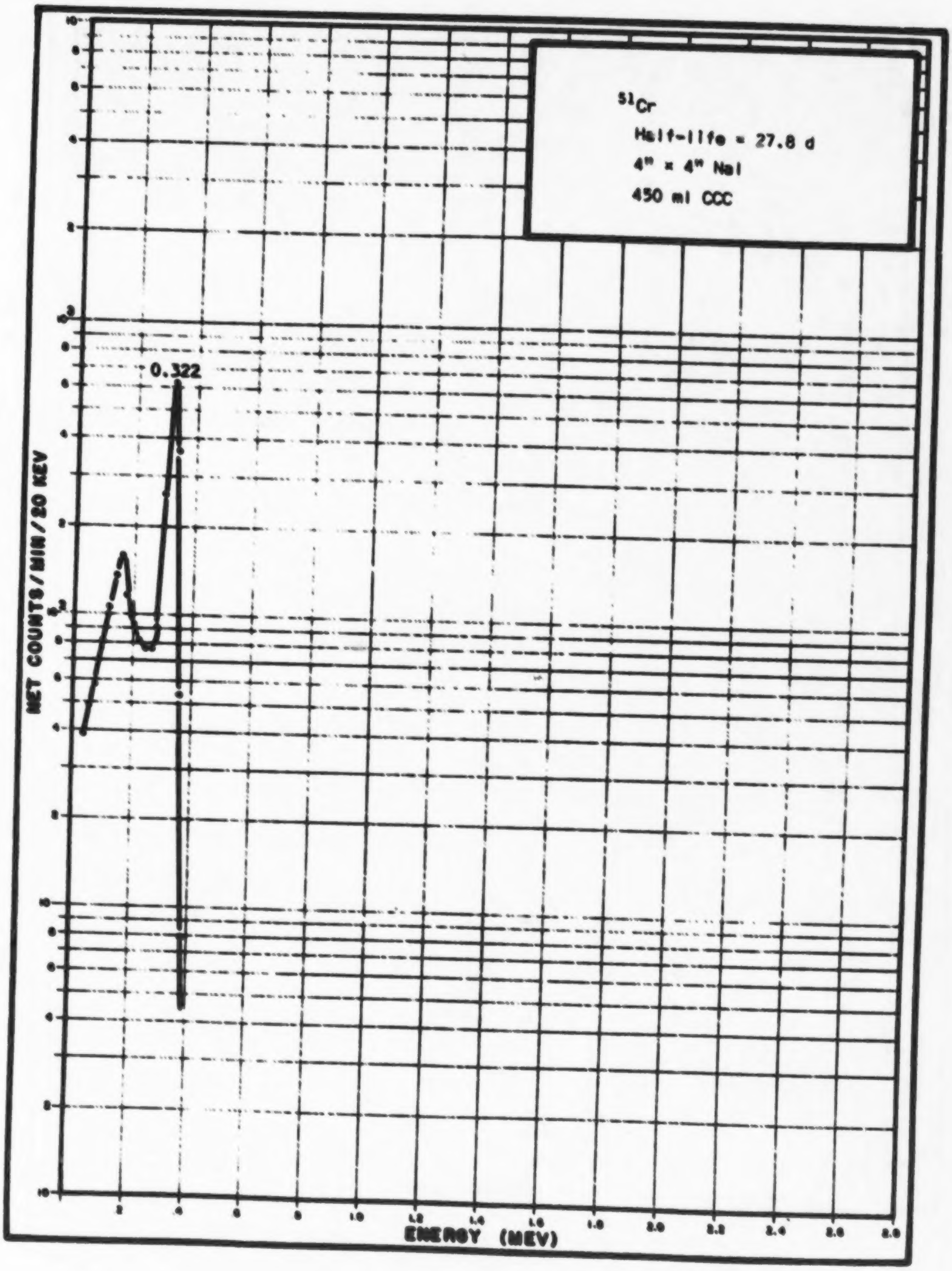


Figure 1.6-6 Gamma spectrum of ^{51}Cr - 450 ml

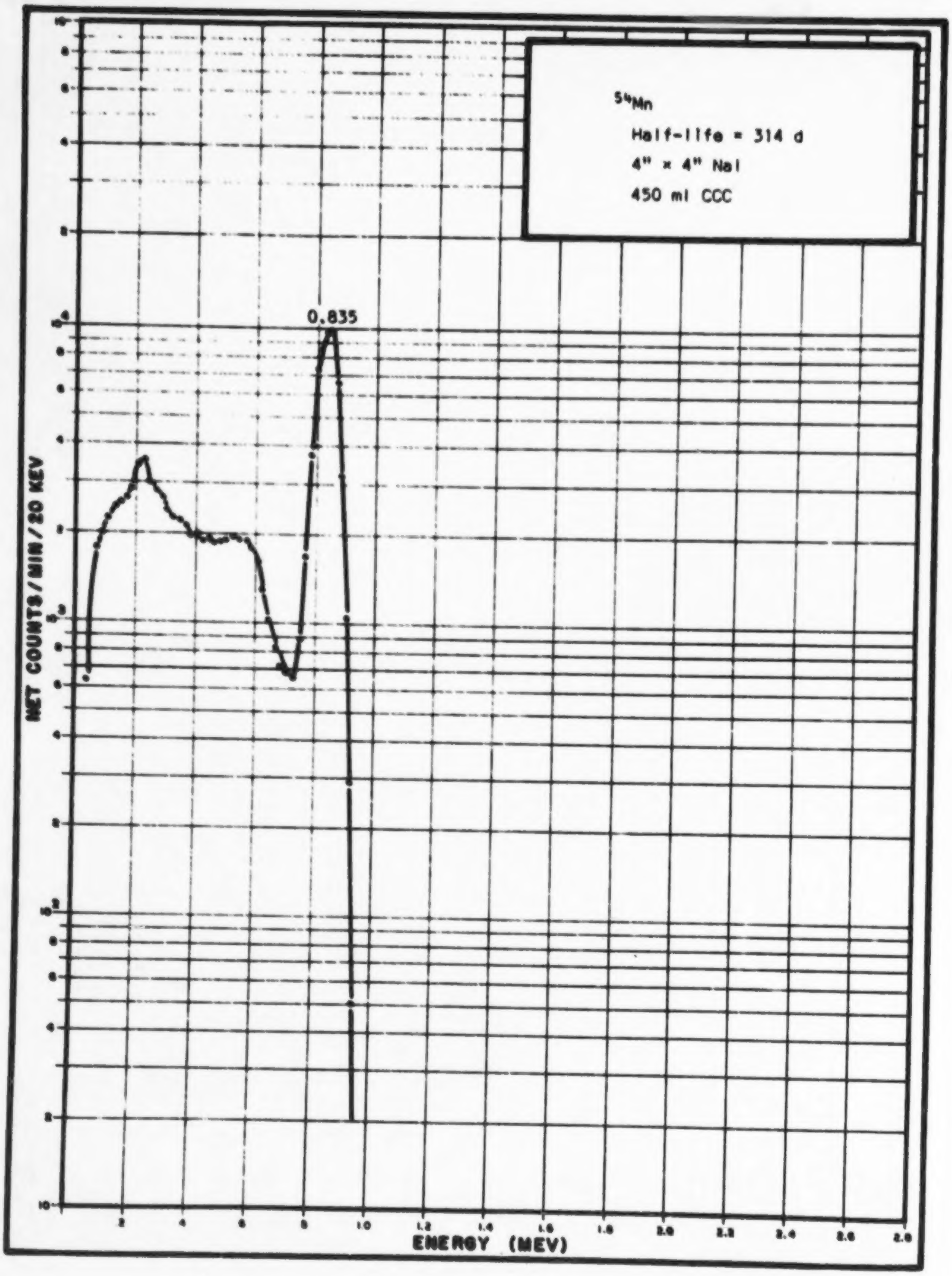


Figure 1.6-7 Gamma spectrum of ^{54}Mn - 450 ml

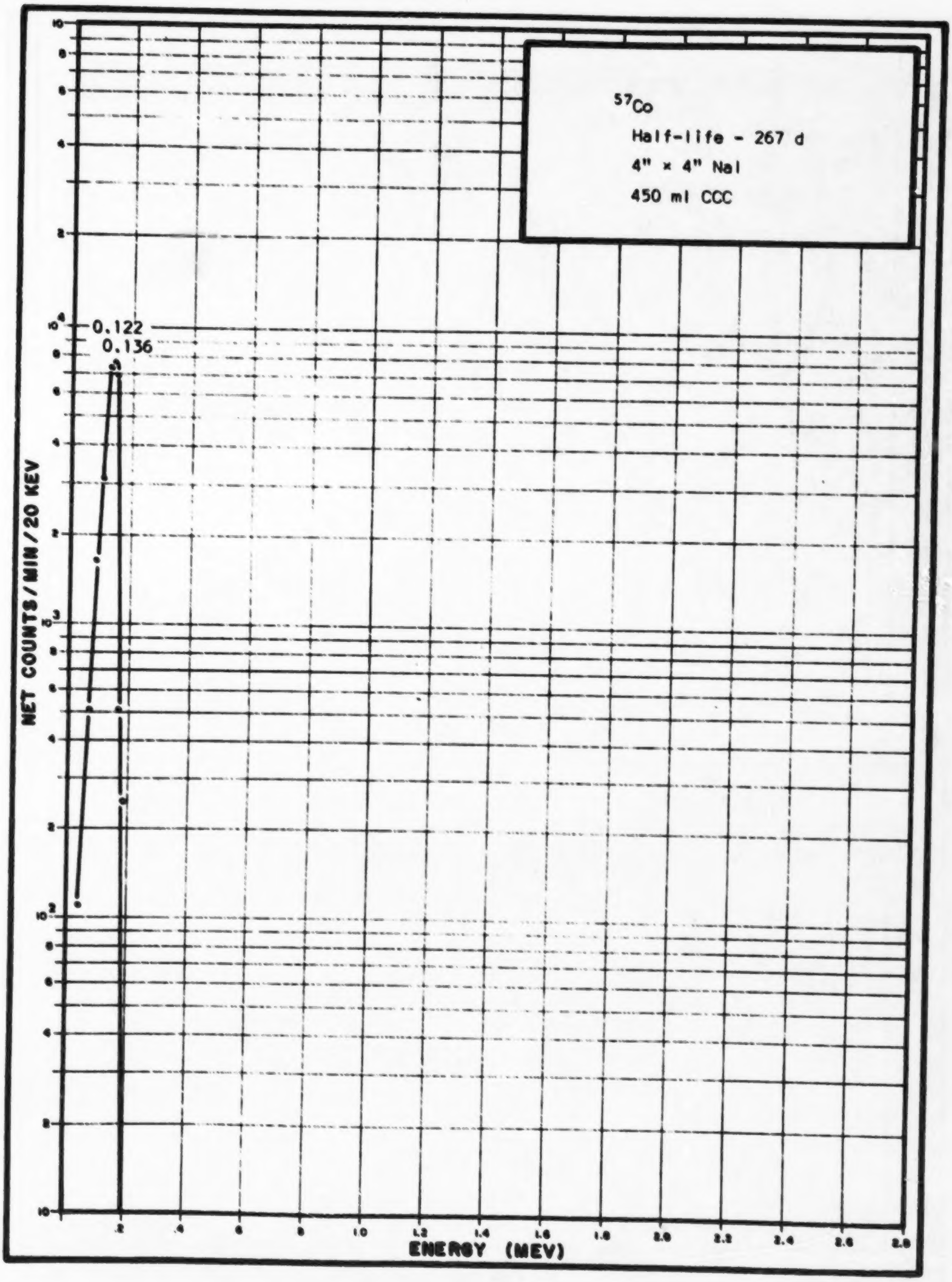


Figure 1.6-8 Gamma spectrum of ^{57}Co - 450 ml

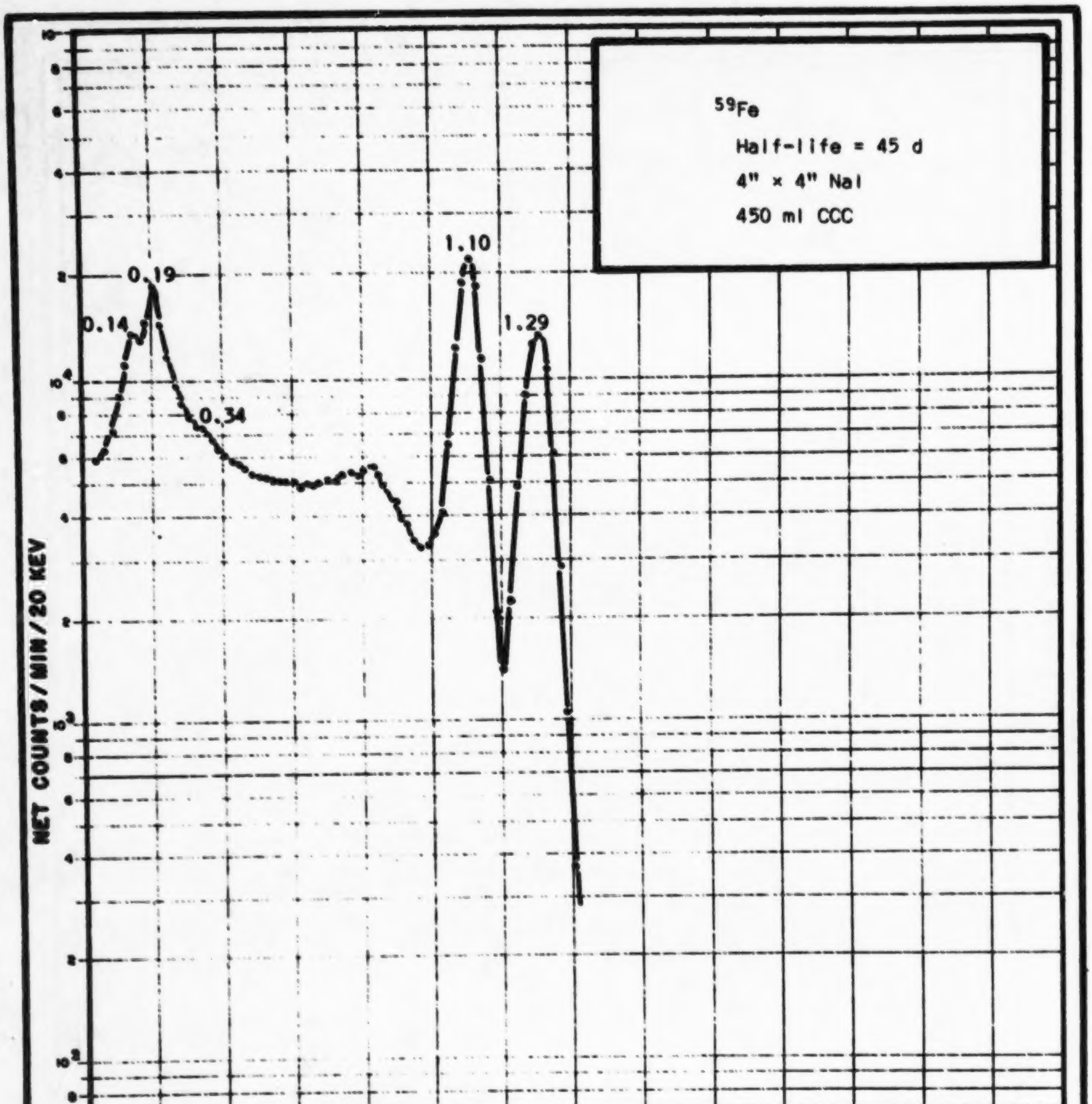


Figure 1.6-9 Gamma spectrum of ^{59}Fe - 450 ml

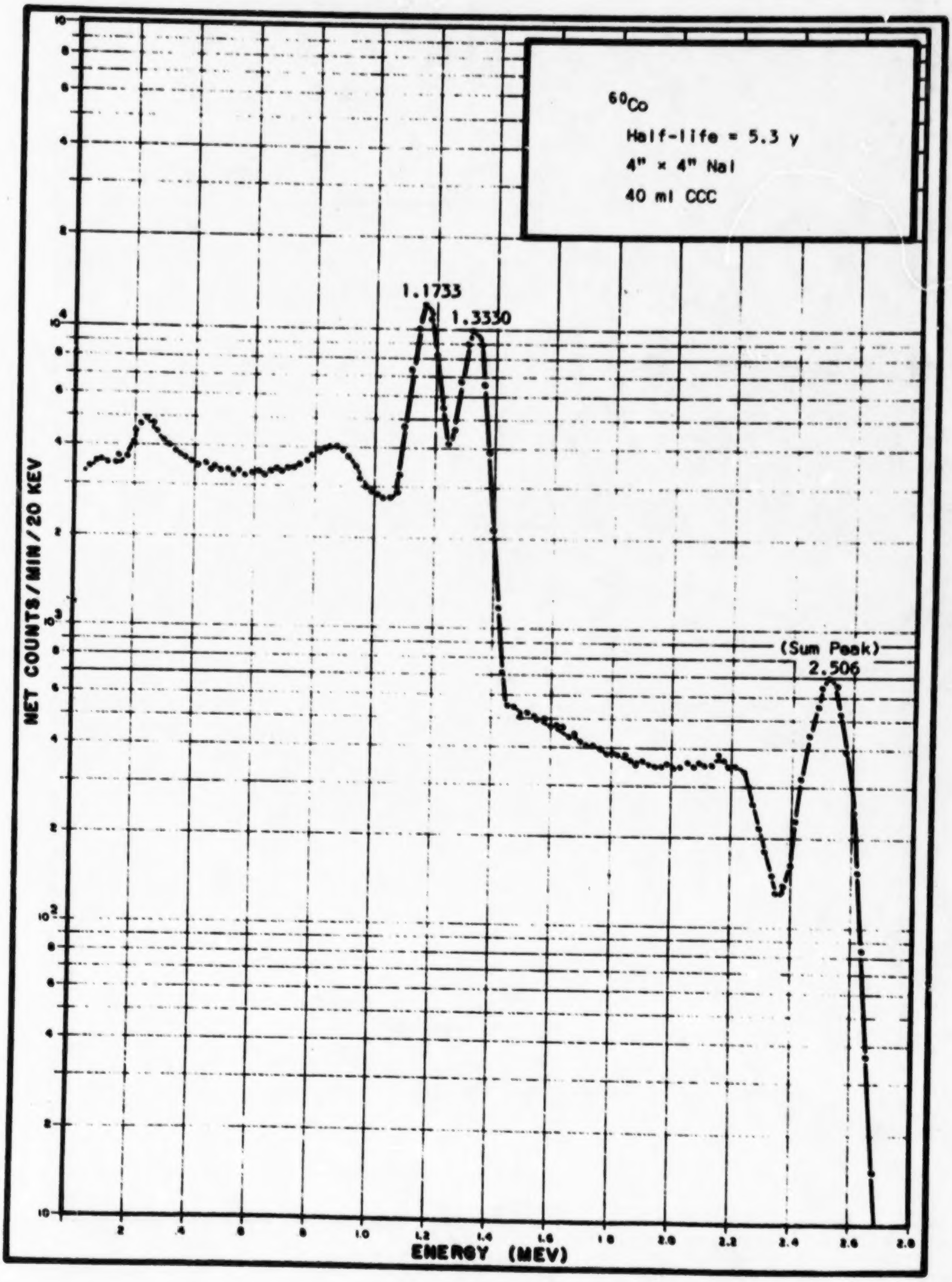


Figure 1.6-10 Gamma spectrum of ^{60}Co - 40 ml

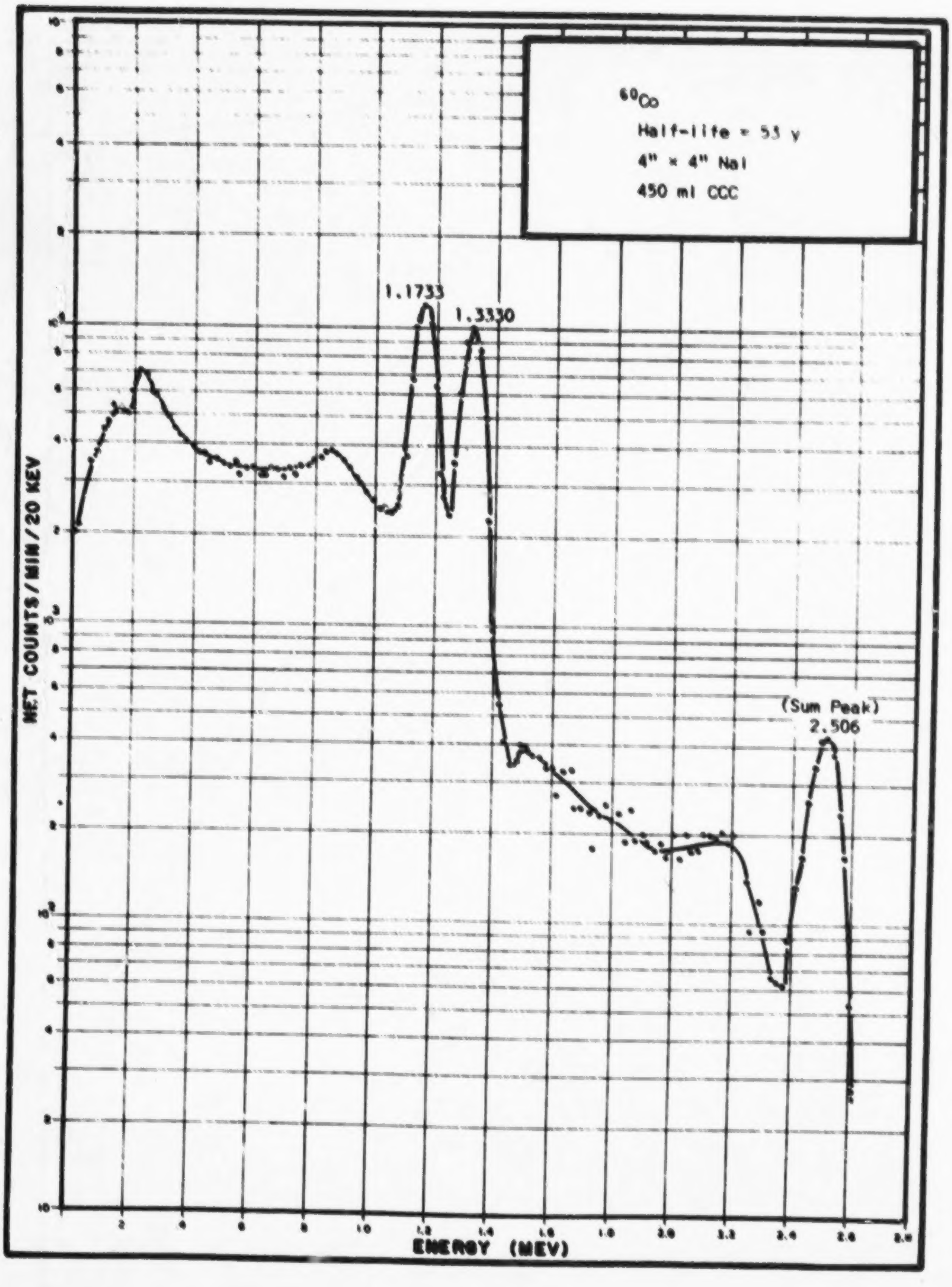


Figure 1.6-11 Gamma spectrum of ^{60}Co - 450 ml

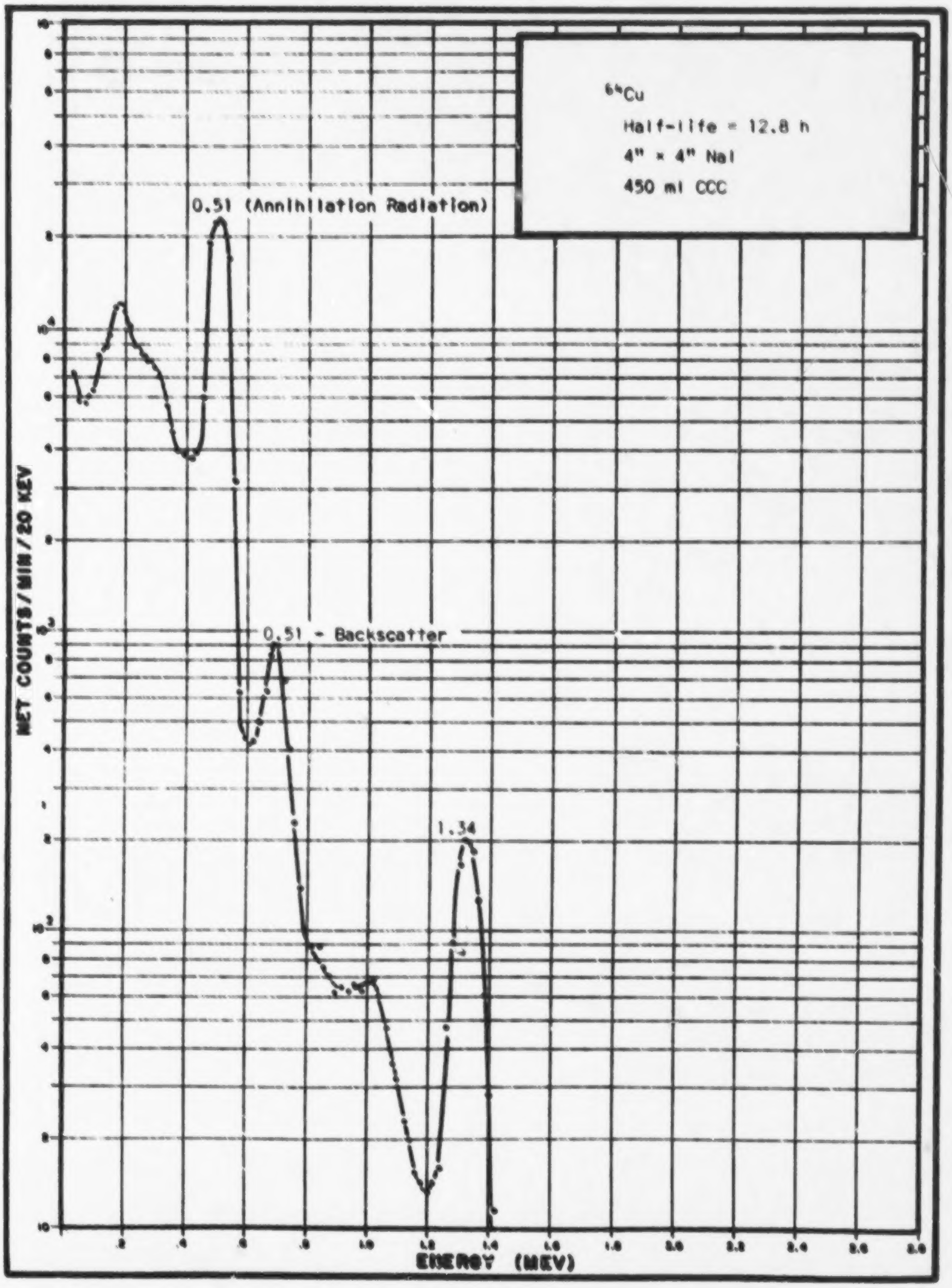


Figure 1.6-12 Gamma spectrum of ^{64}Cu - 450 ml

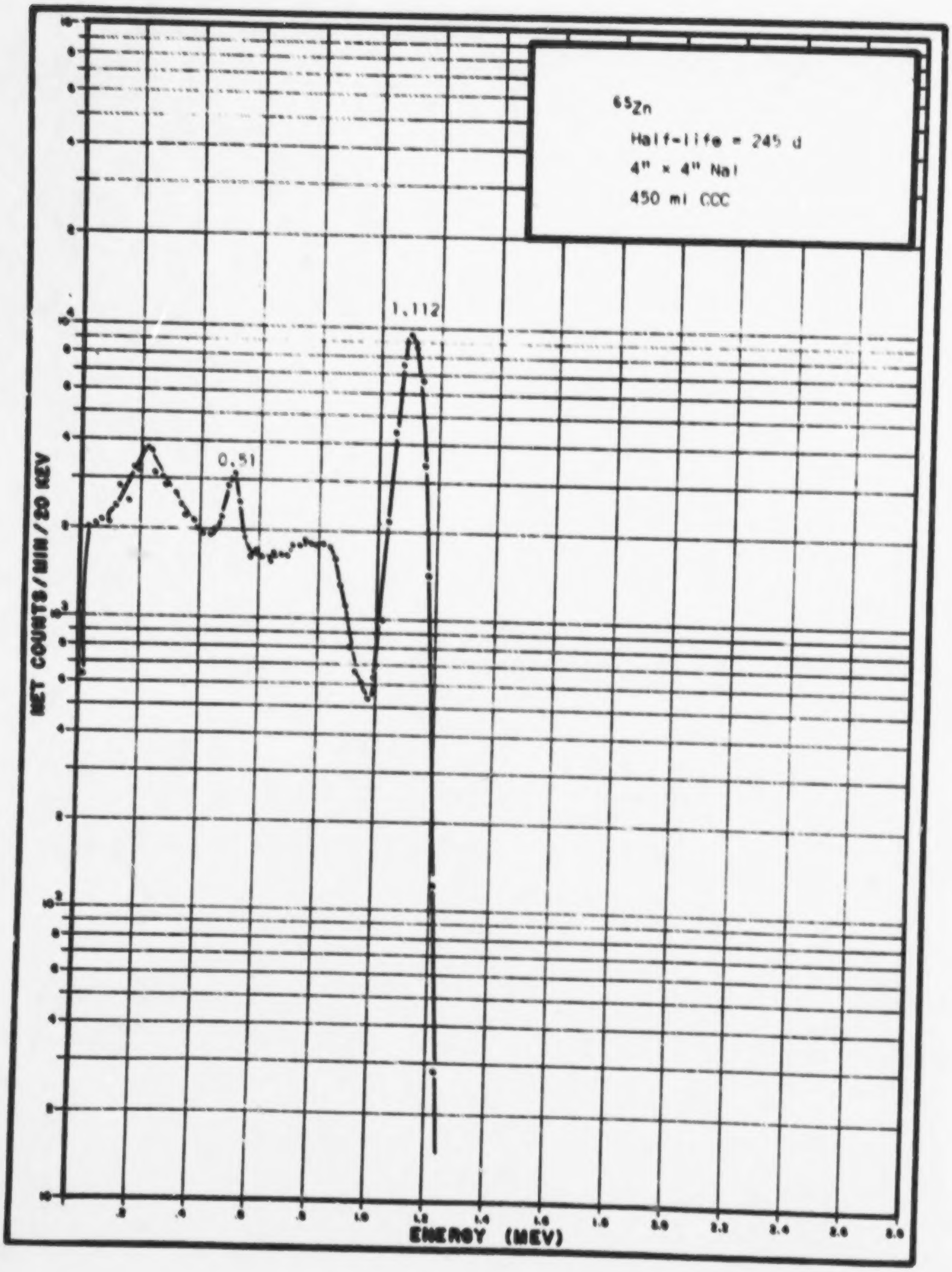


Figure 1.6-13 Gamma spectrum of ^{65}Zn - 450 ml

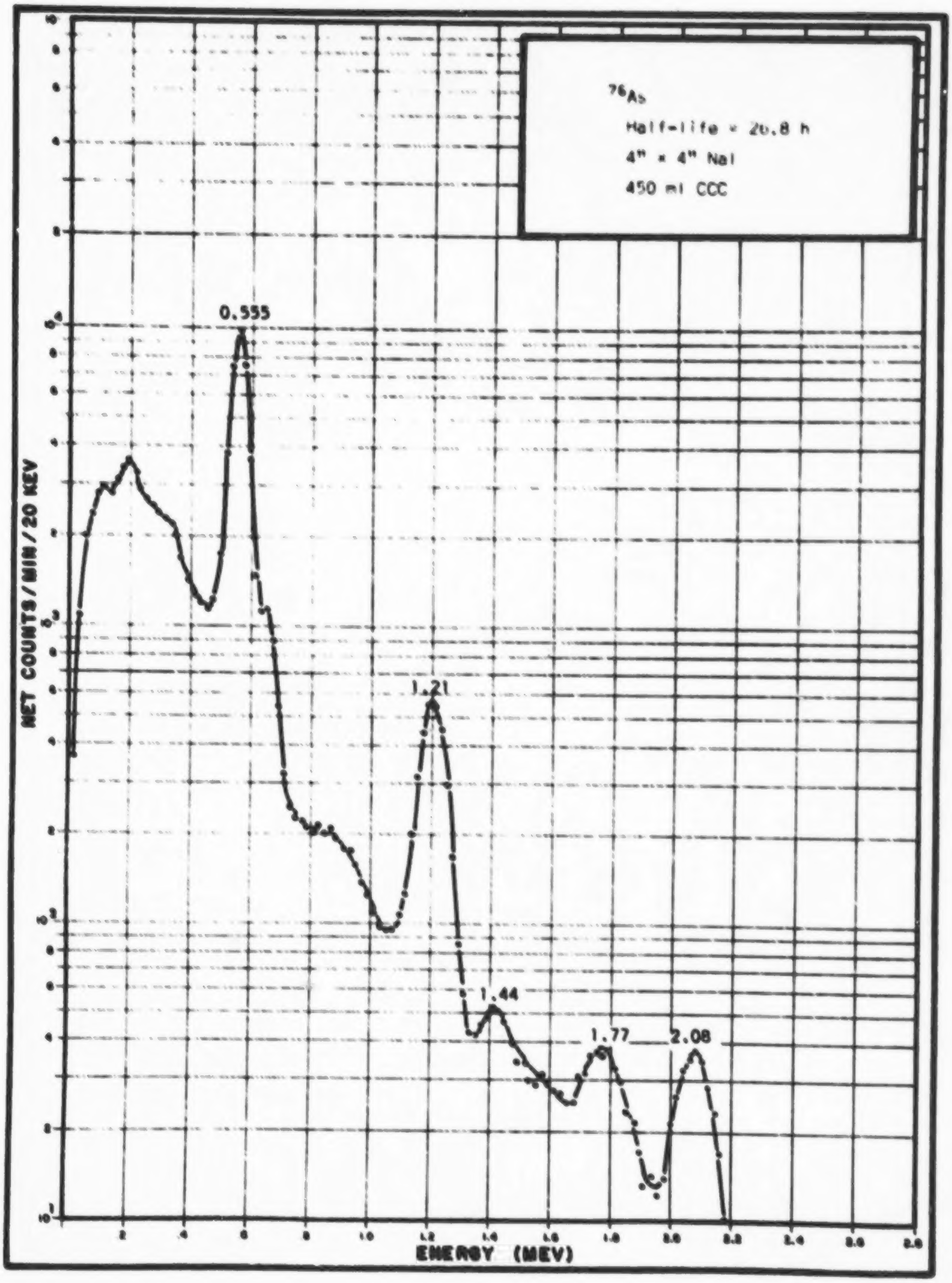


Figure 1.6-14 Gamma spectrum of ^{76}As - 450 ml

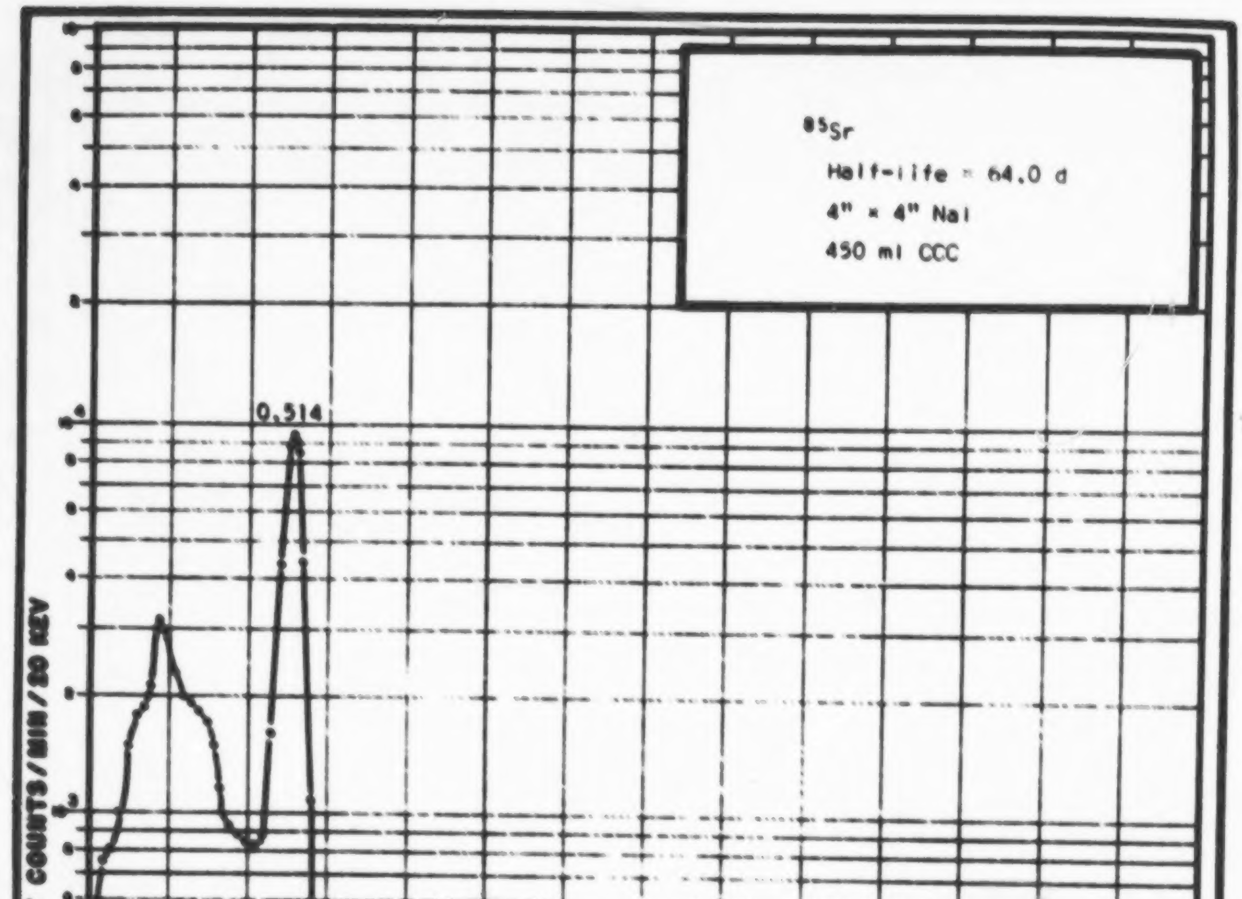


Figure 1.6-15 Gamma spectrum of ^{85}Sr - 450 ml

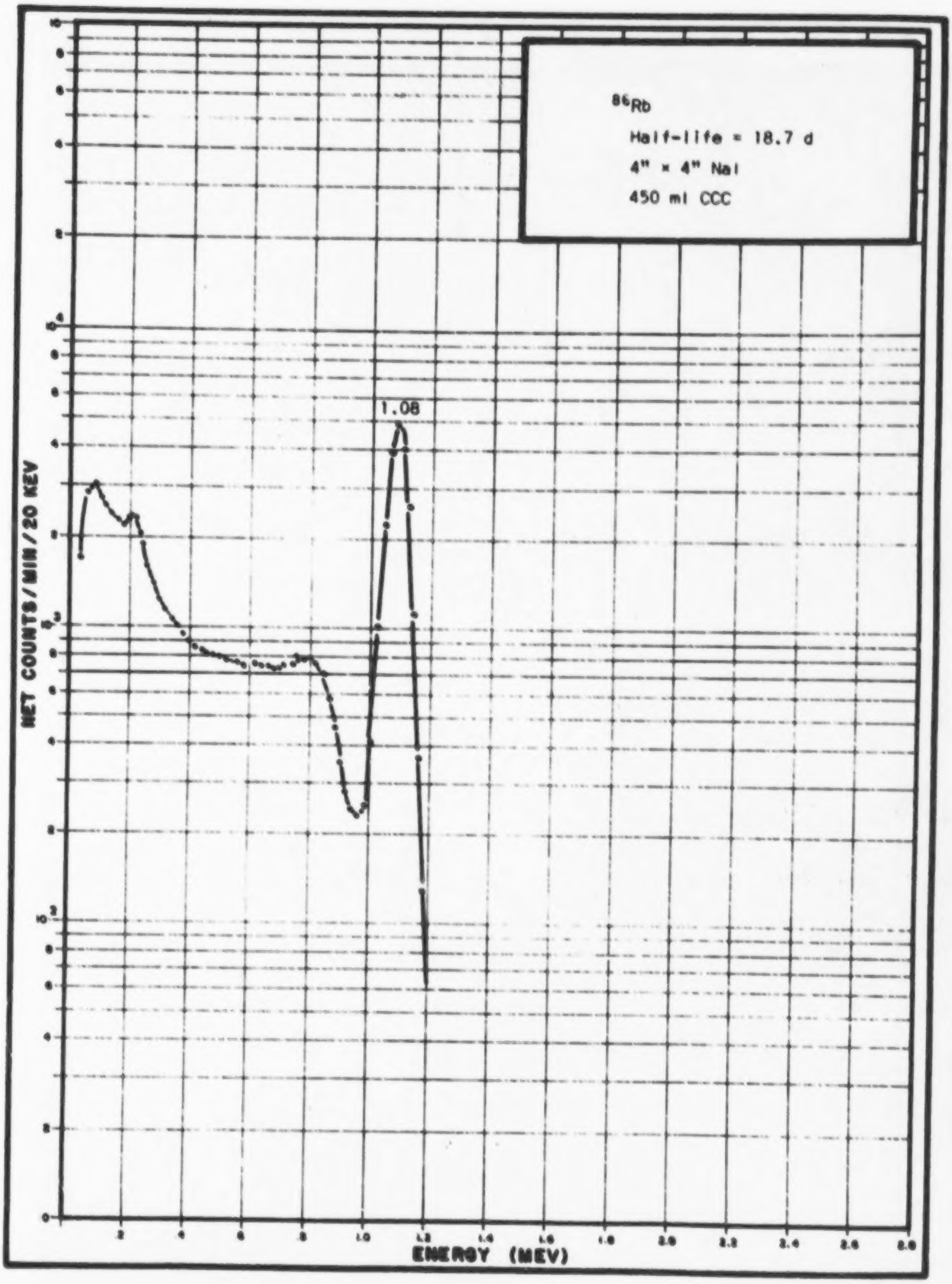


Figure 1.6-16 Gamma spectrum of ^{86}Rb - 450 ml

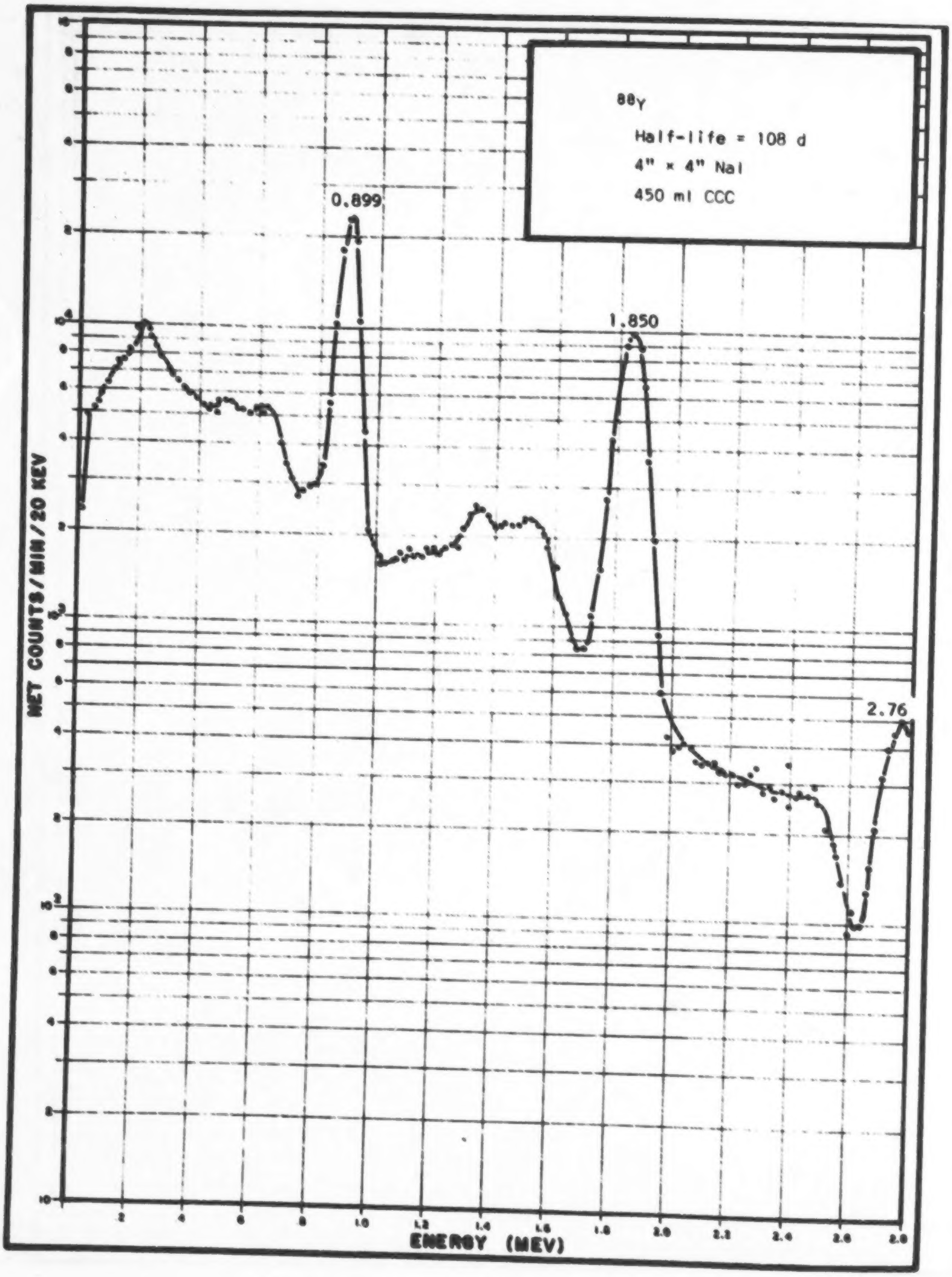


Figure 1.6-17 Gamma spectrum of ^{88}Y - 450 ml

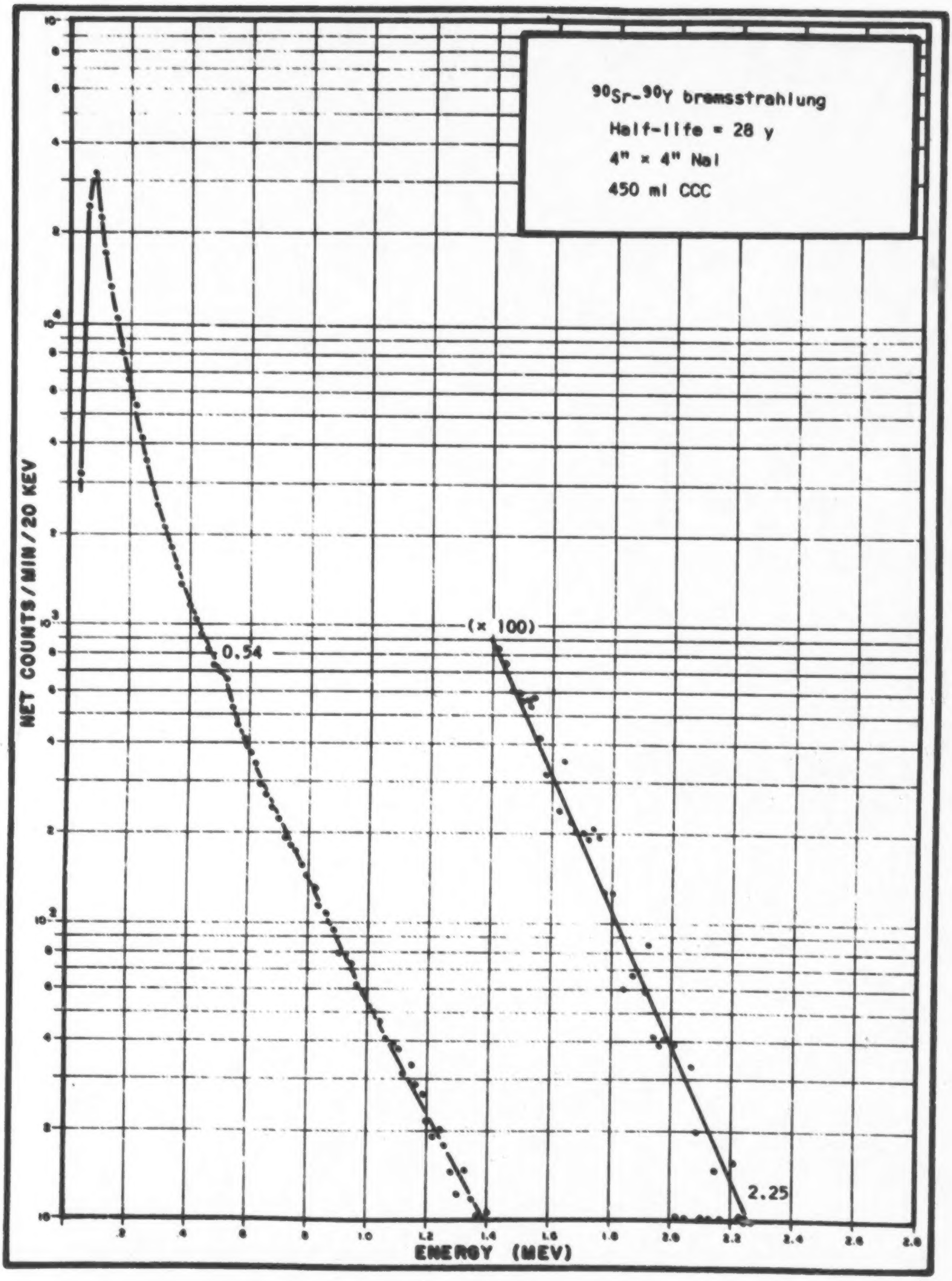


Figure 1.6-18 Gamma spectrum of $^{90}Sr-^{90}Y$ bremsstrahlung - 450 ml

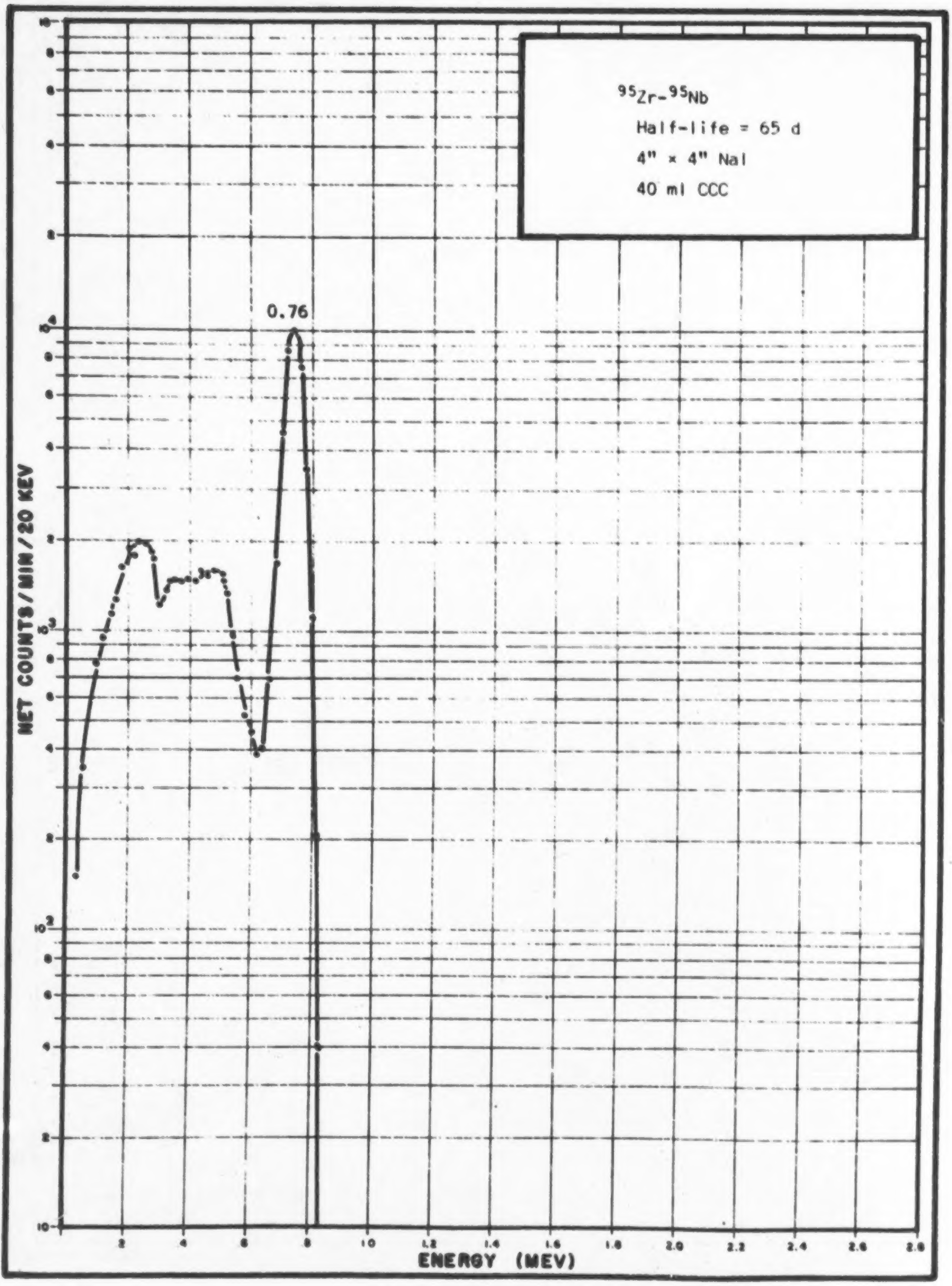


Figure 1.6-19 Gamma spectrum of ^{95}Zr-^{95}Nb - 40 ml

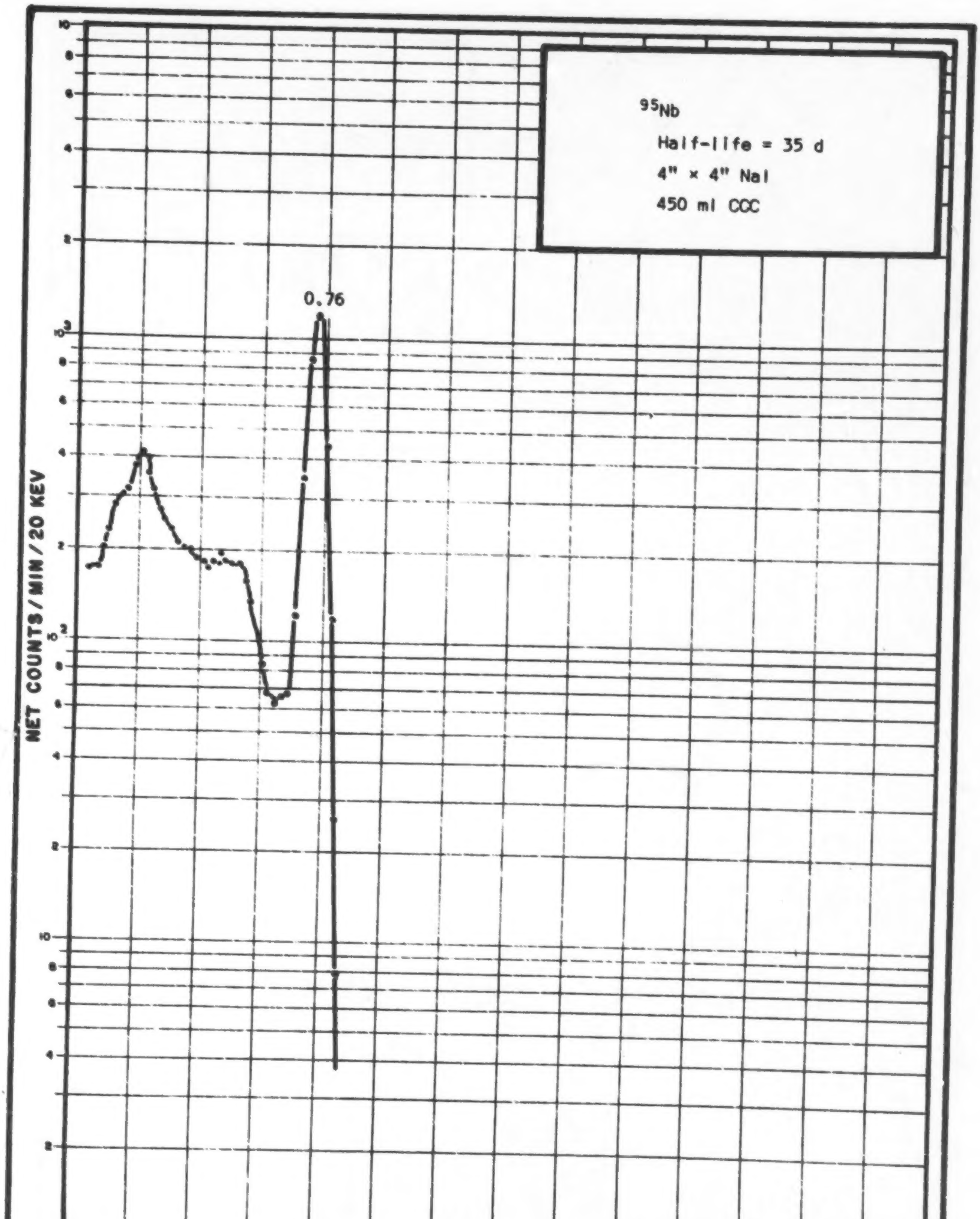


Figure 1.6-20 Gamma spectrum of ^{95}Nb - 450 ml

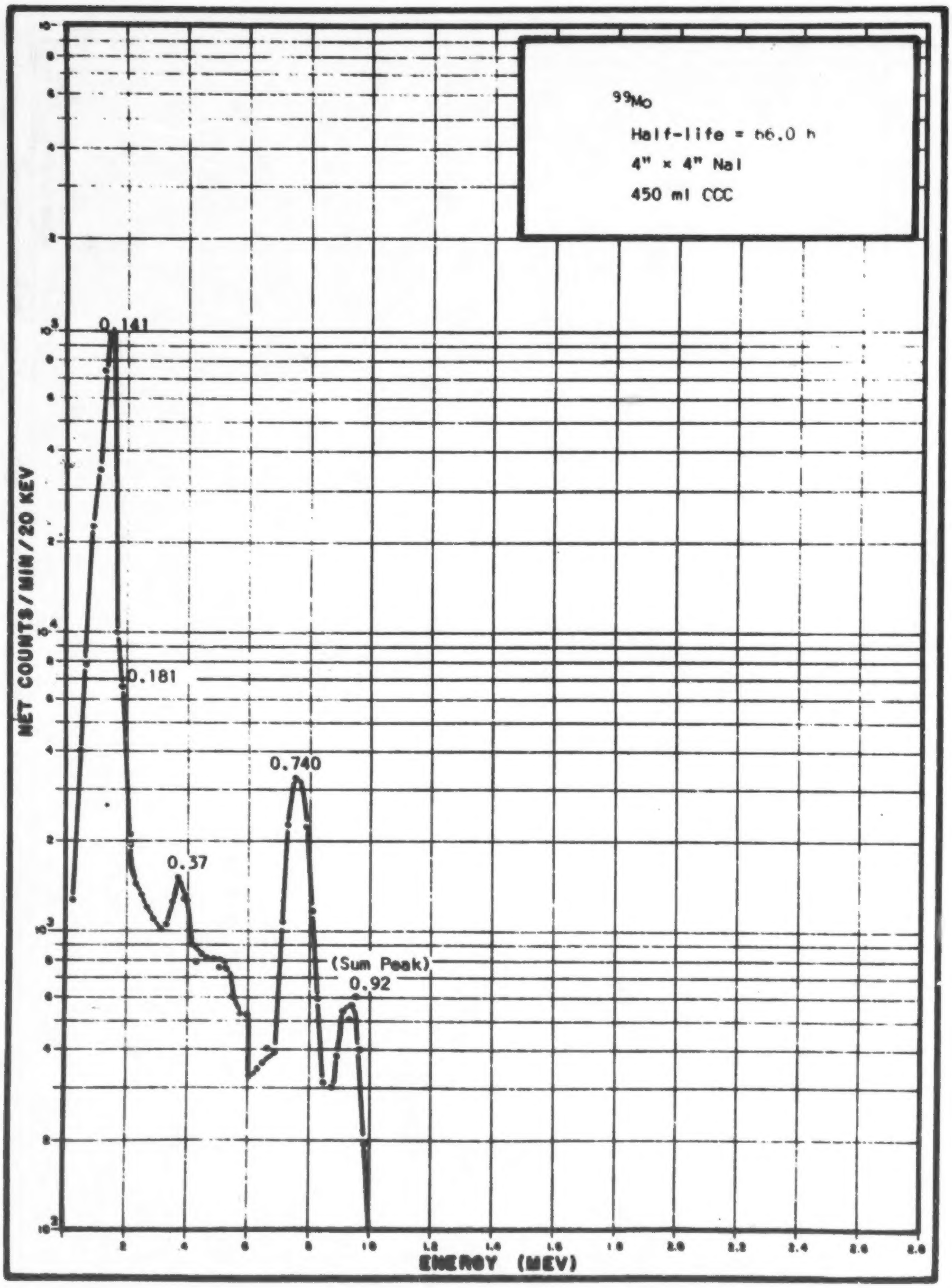


Figure 1.6-21 Gamma spectrum of ^{99}Mo - 450 ml

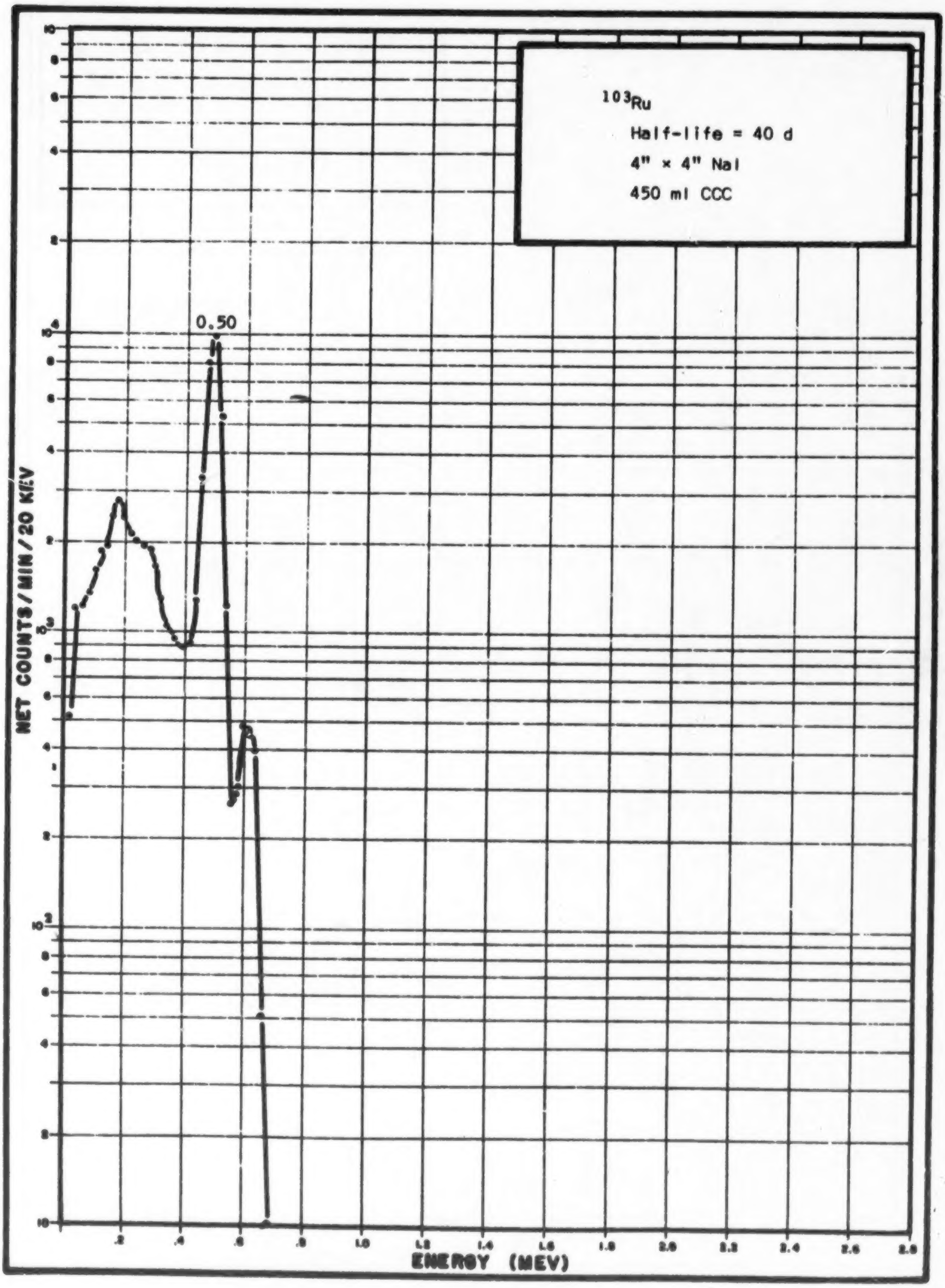


Figure 1.6-22 Gamma spectrum of ^{103}Ru - 450 ml

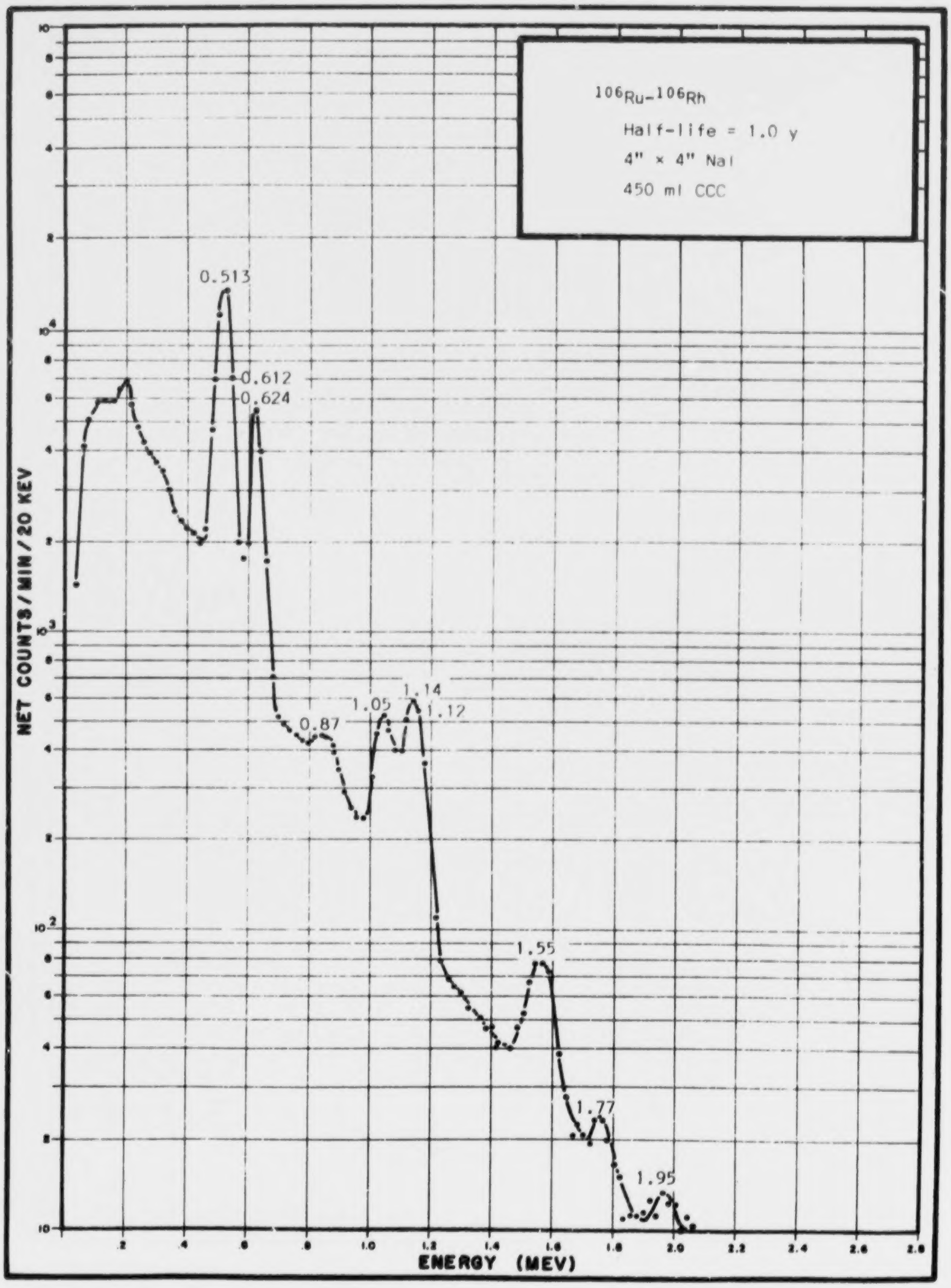


Figure 1.6-23 Gamma spectrum of ^{106}Ru-^{106}Rh - 450 ml

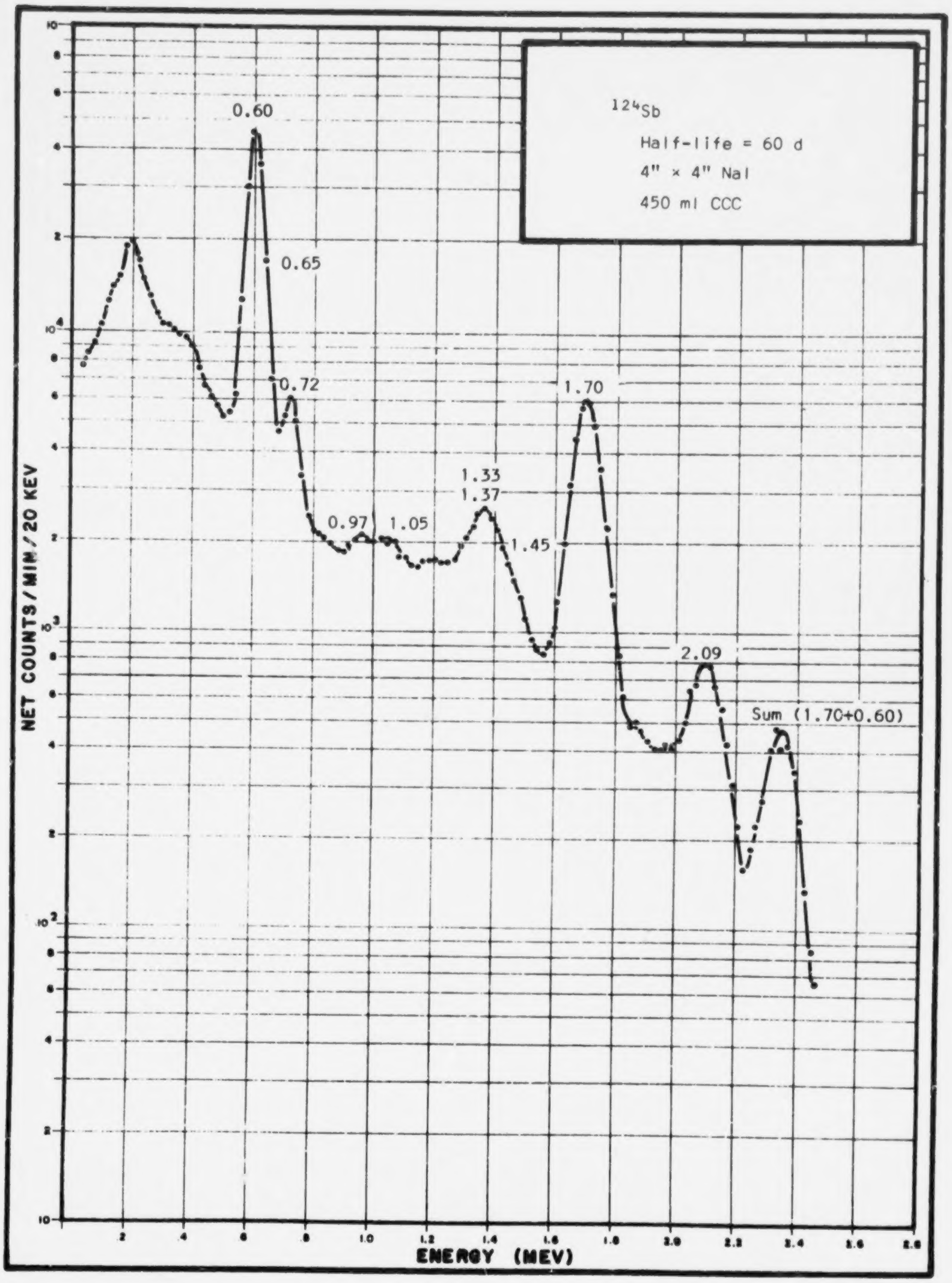


Figure 1.6-24 Gamma spectrum of ^{124}Sb - 450 ml

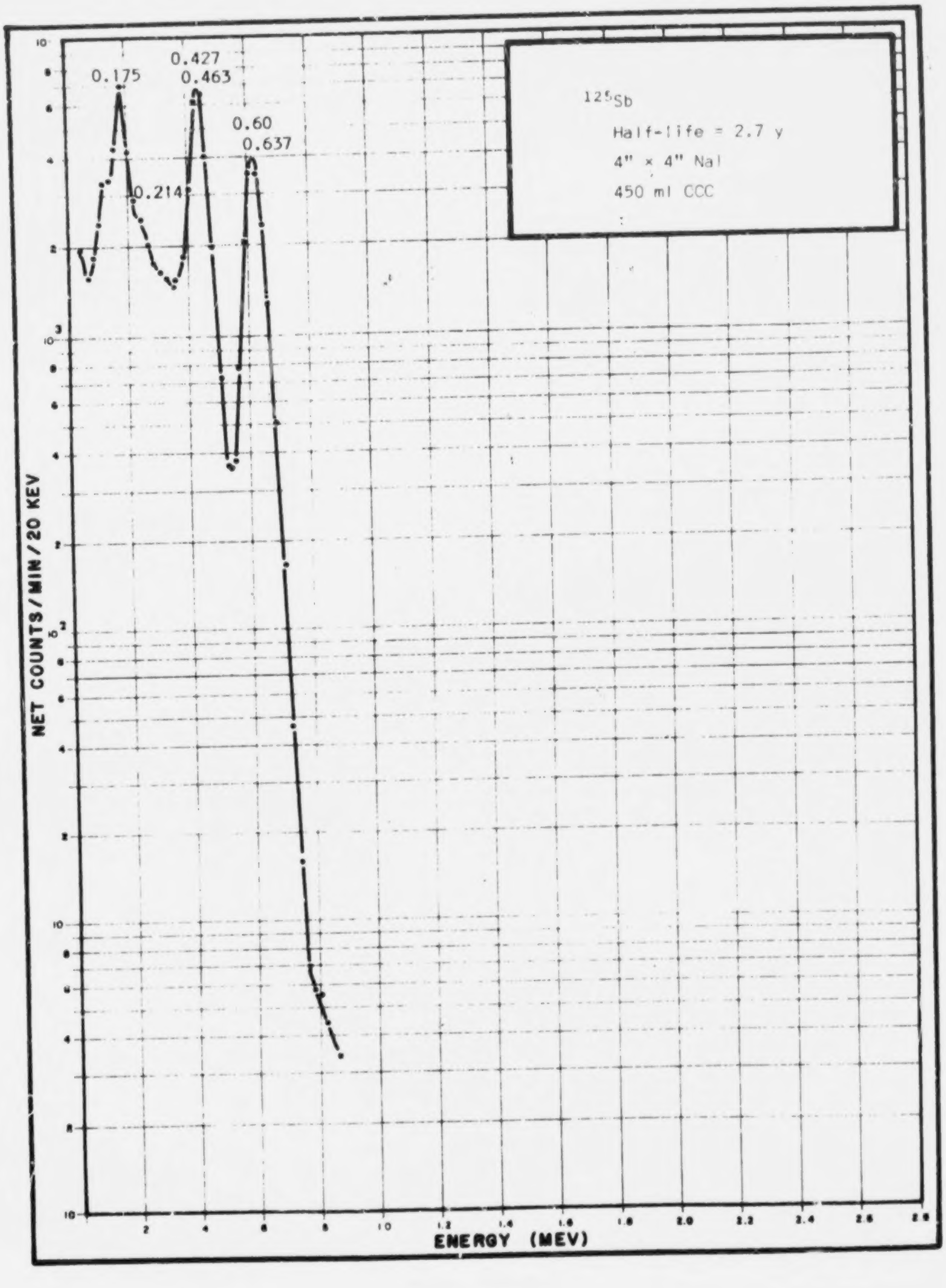


Figure 1.6-25 Gamma spectrum of ^{125}Sb - 450 ml

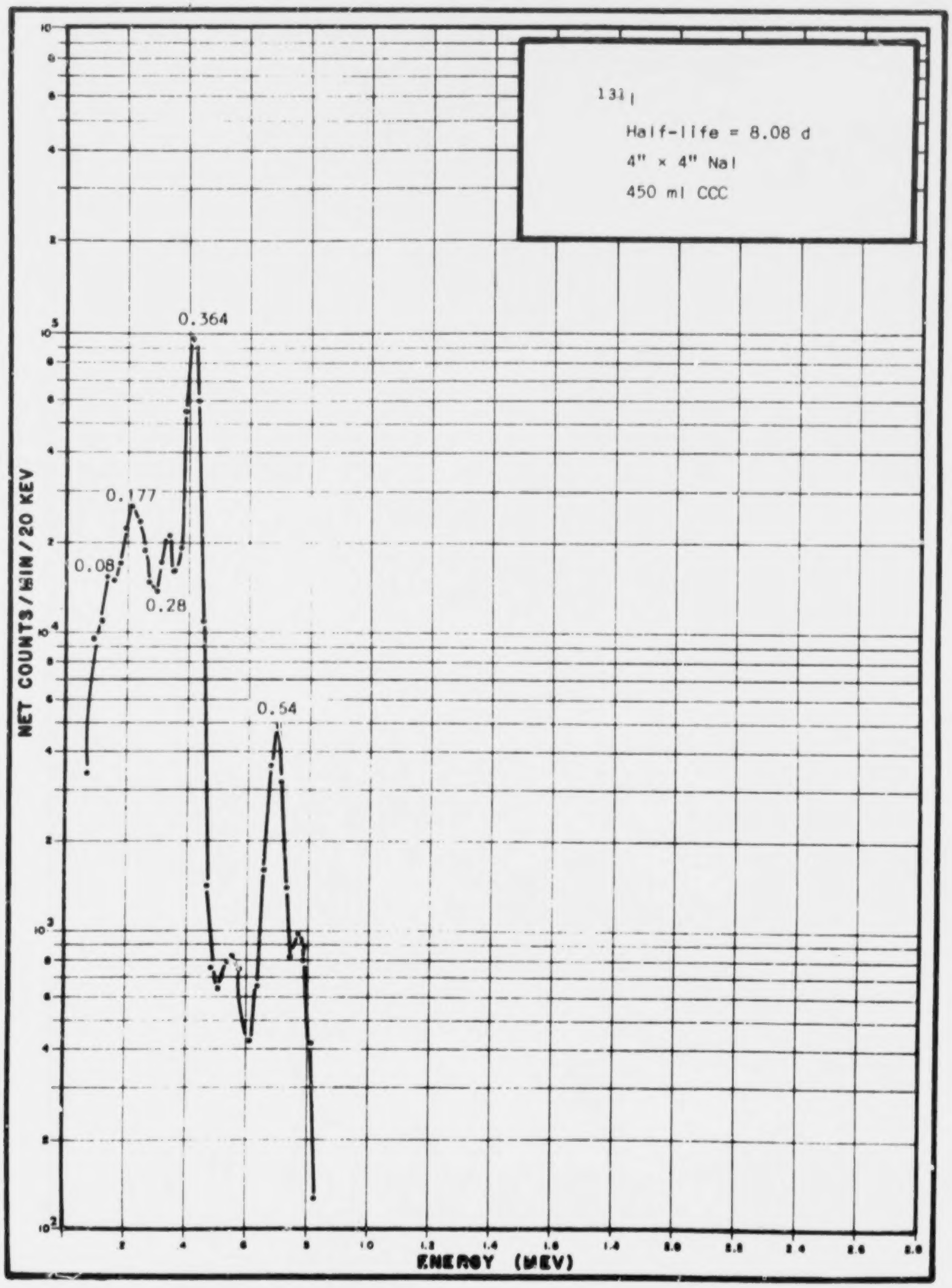


Figure 1.6-26 Gamma spectrum of ^{131}I - 450 ml

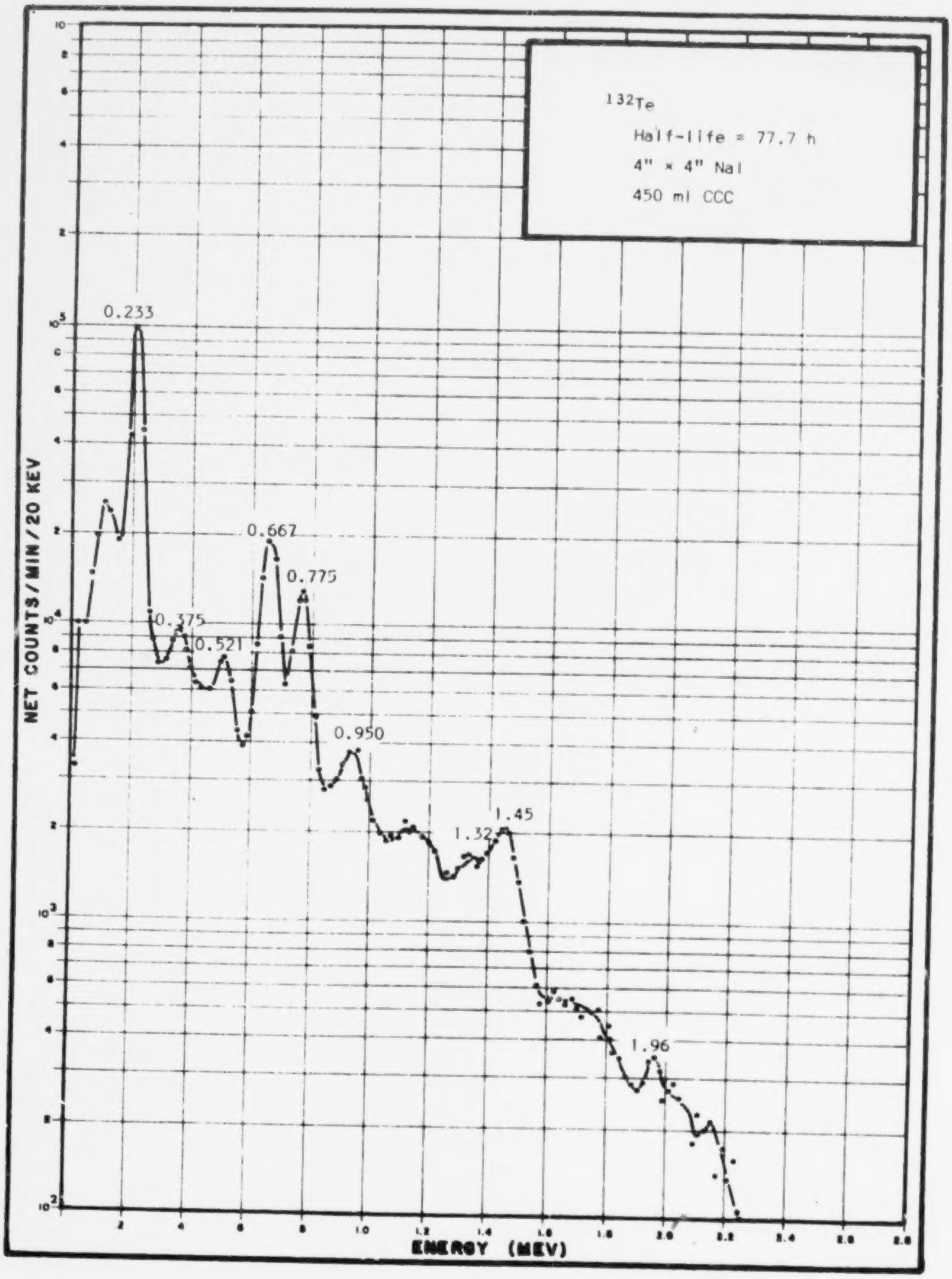


Figure 1.6-27 Gamma spectrum of ^{132}Te - 450 ml

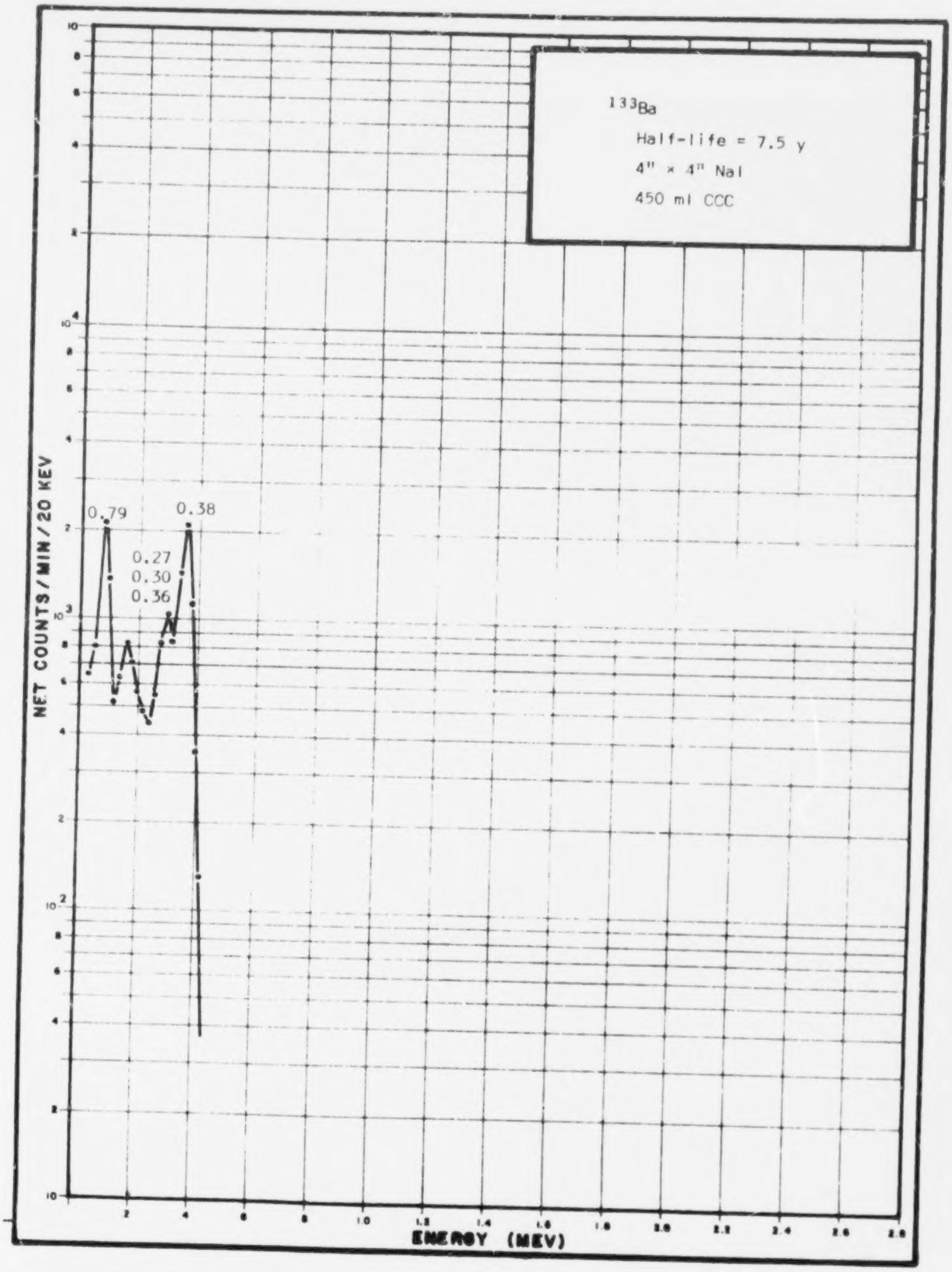


Figure 1.6-28 Gamma spectrum of ^{133}Ba - 450 ml

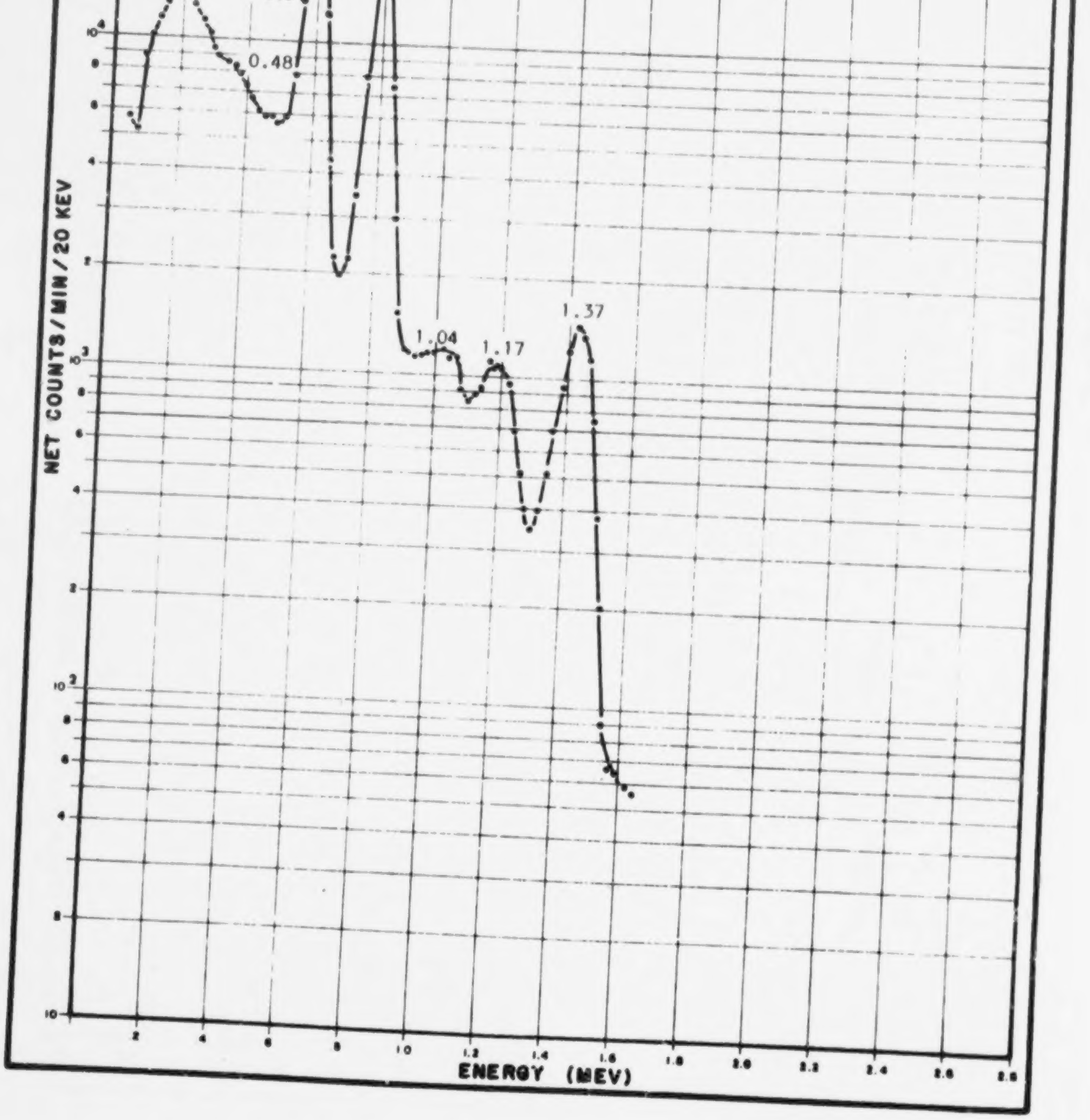


Figure 1.6-29 Gamma spectrum of ^{134}Cs - 450 ml

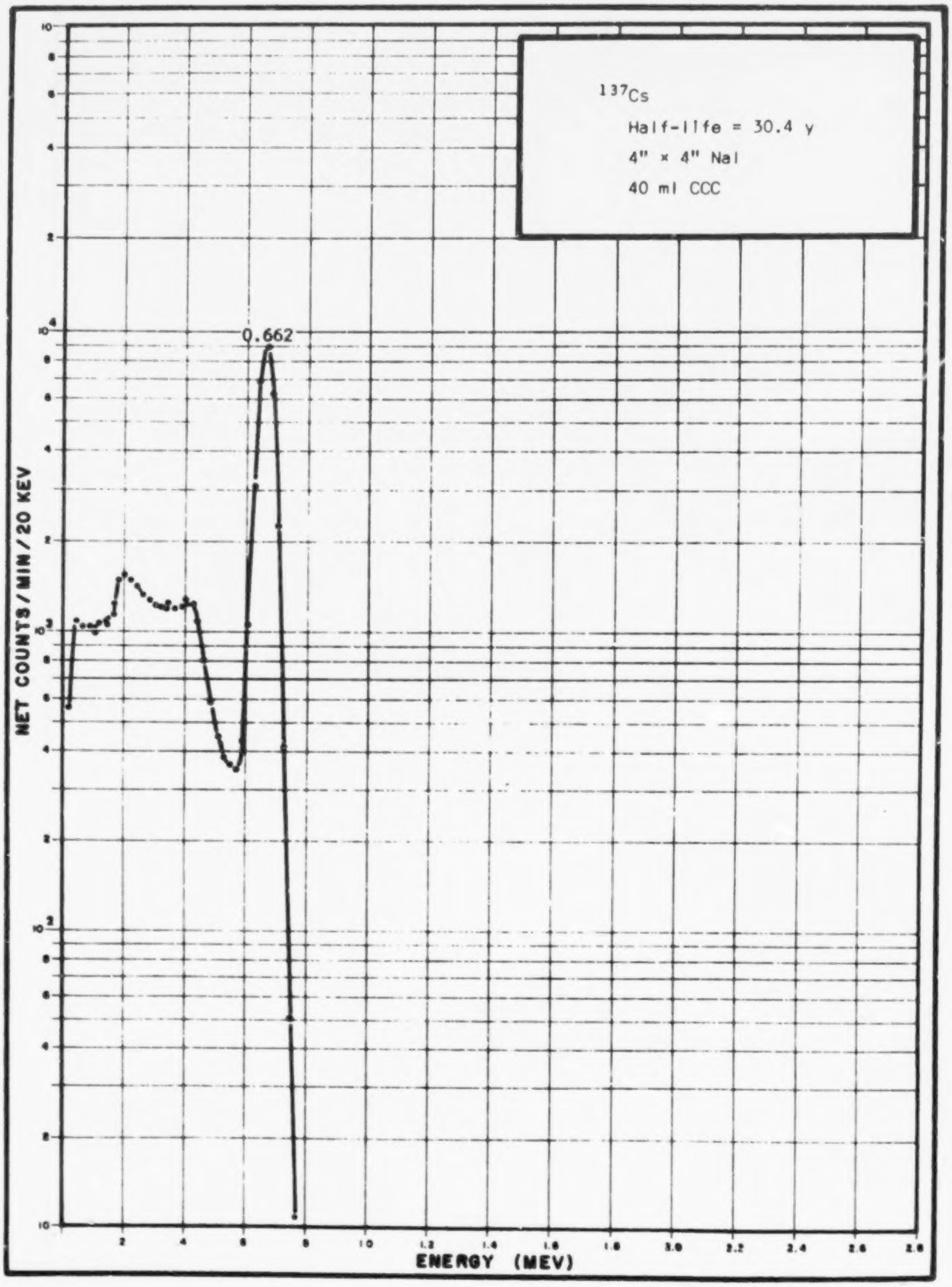


Figure 1.6-30 Gamma spectrum of ^{137}Cs - 40 ml

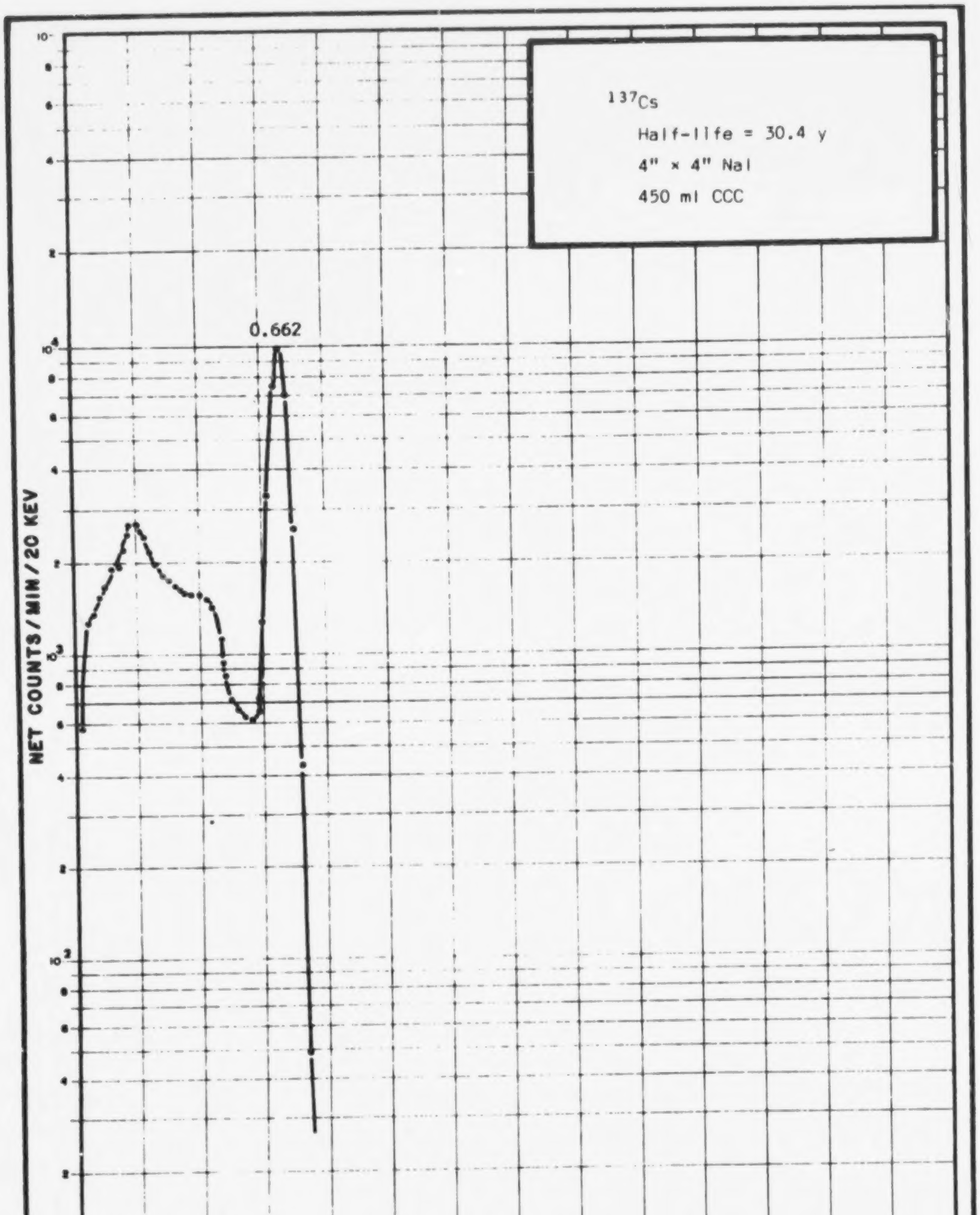


Figure 1.6-31 Gamma spectrum of ^{137}Cs - 450 ml

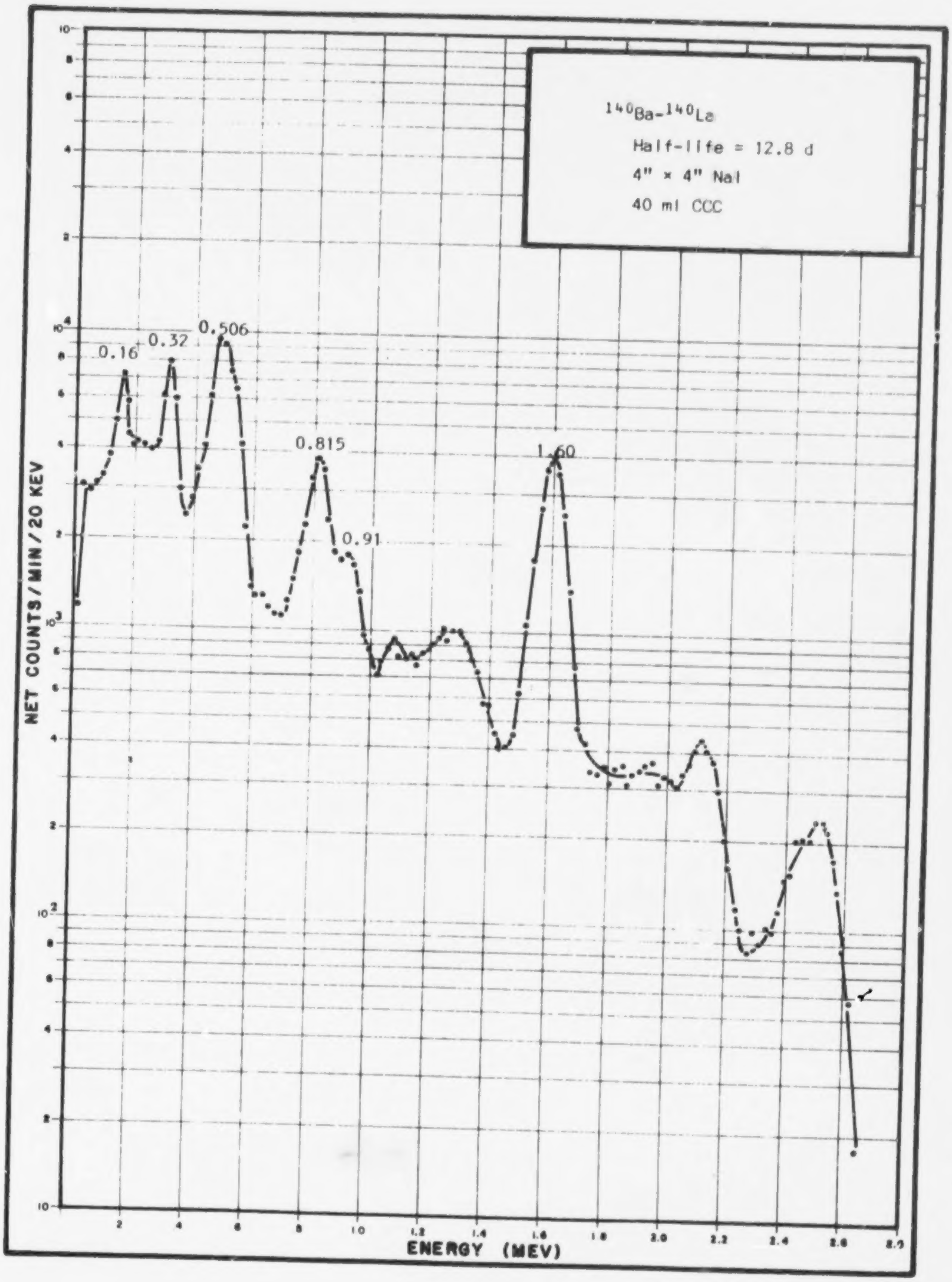


Figure 1.6-32 Gamma spectrum of ^{140}Ba-^{140}La - 40 ml

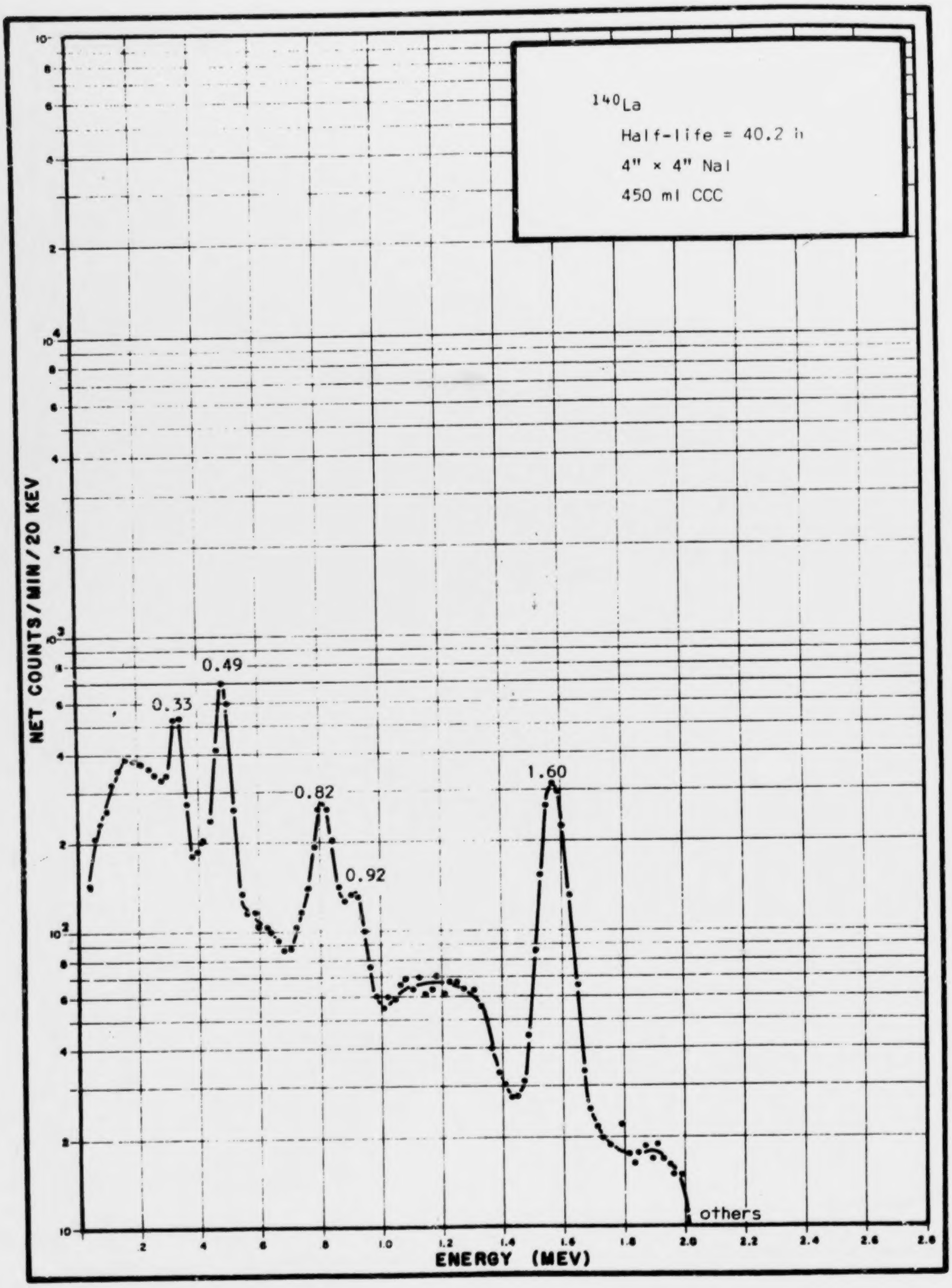


Figure 1.6-33 Gamma spectrum of ^{140}La - 450 ml

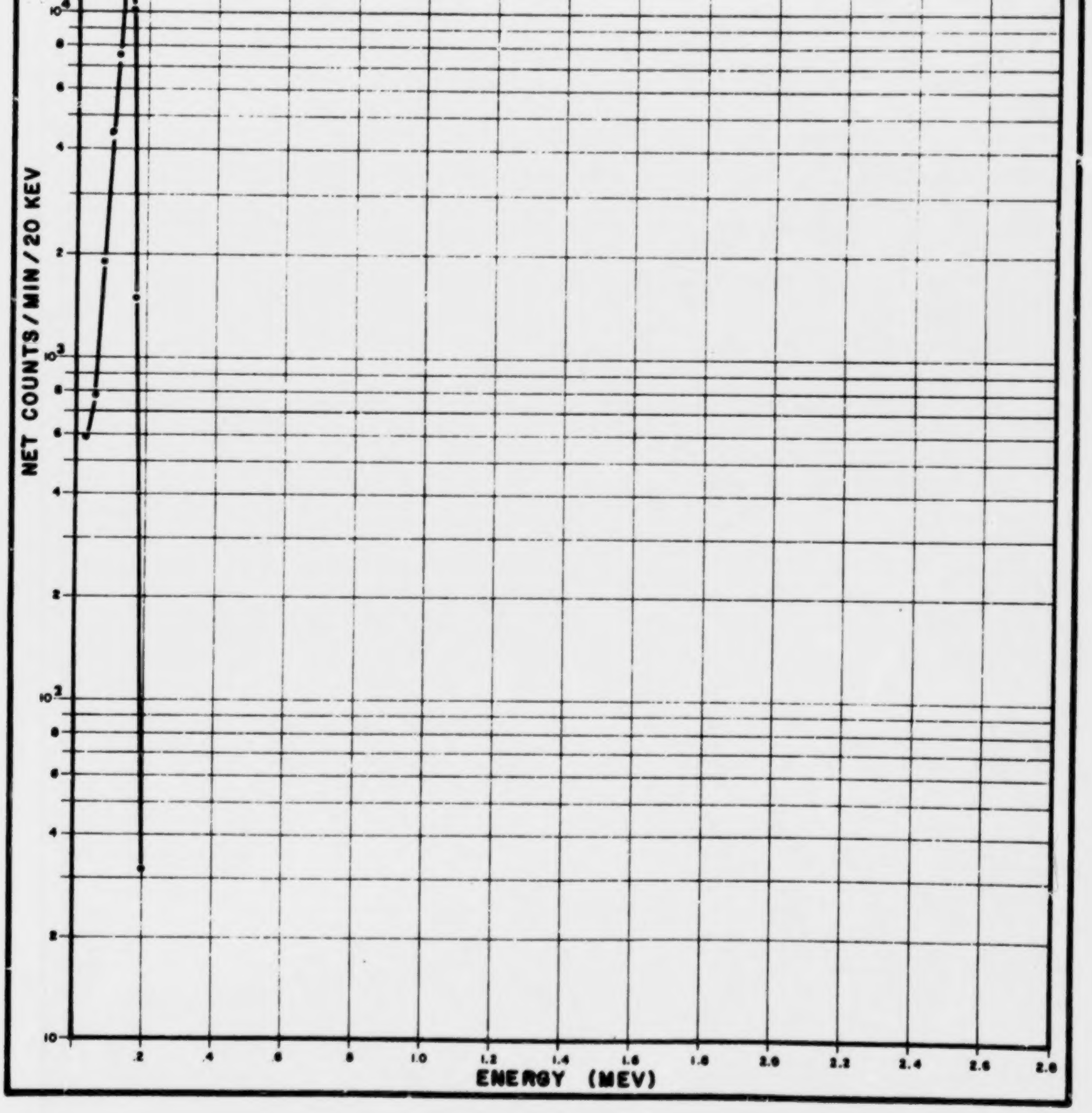


Figure 1.6-34 Gamma spectrum of ^{141}Ce - 450 ml

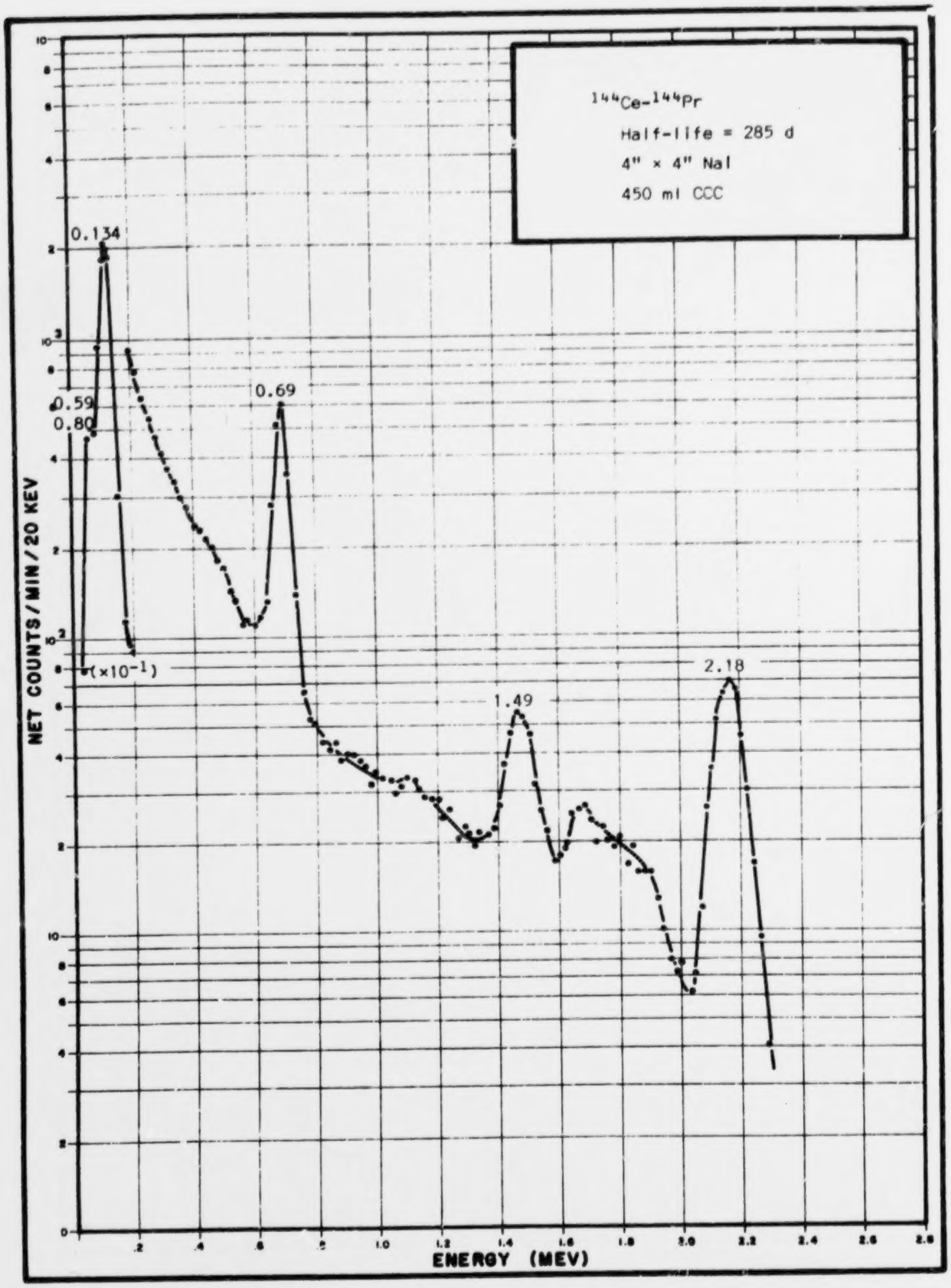


Figure 1.6-35 Gamma spectrum of ^{144}Ce-^{144}Pr - 450 ml

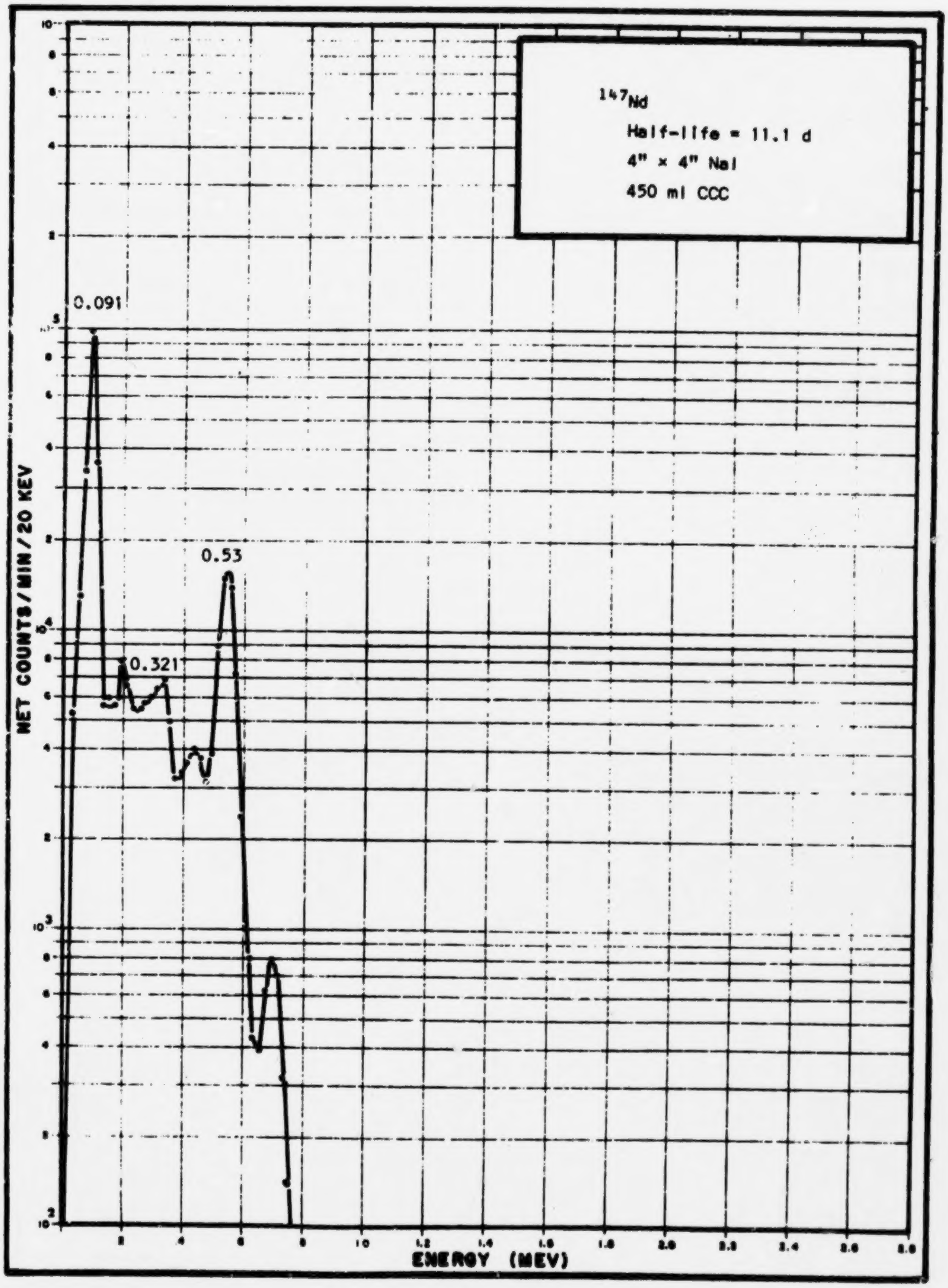


Figure 1.6-36 Gamma spectrum of ^{147}Nd - 450 ml

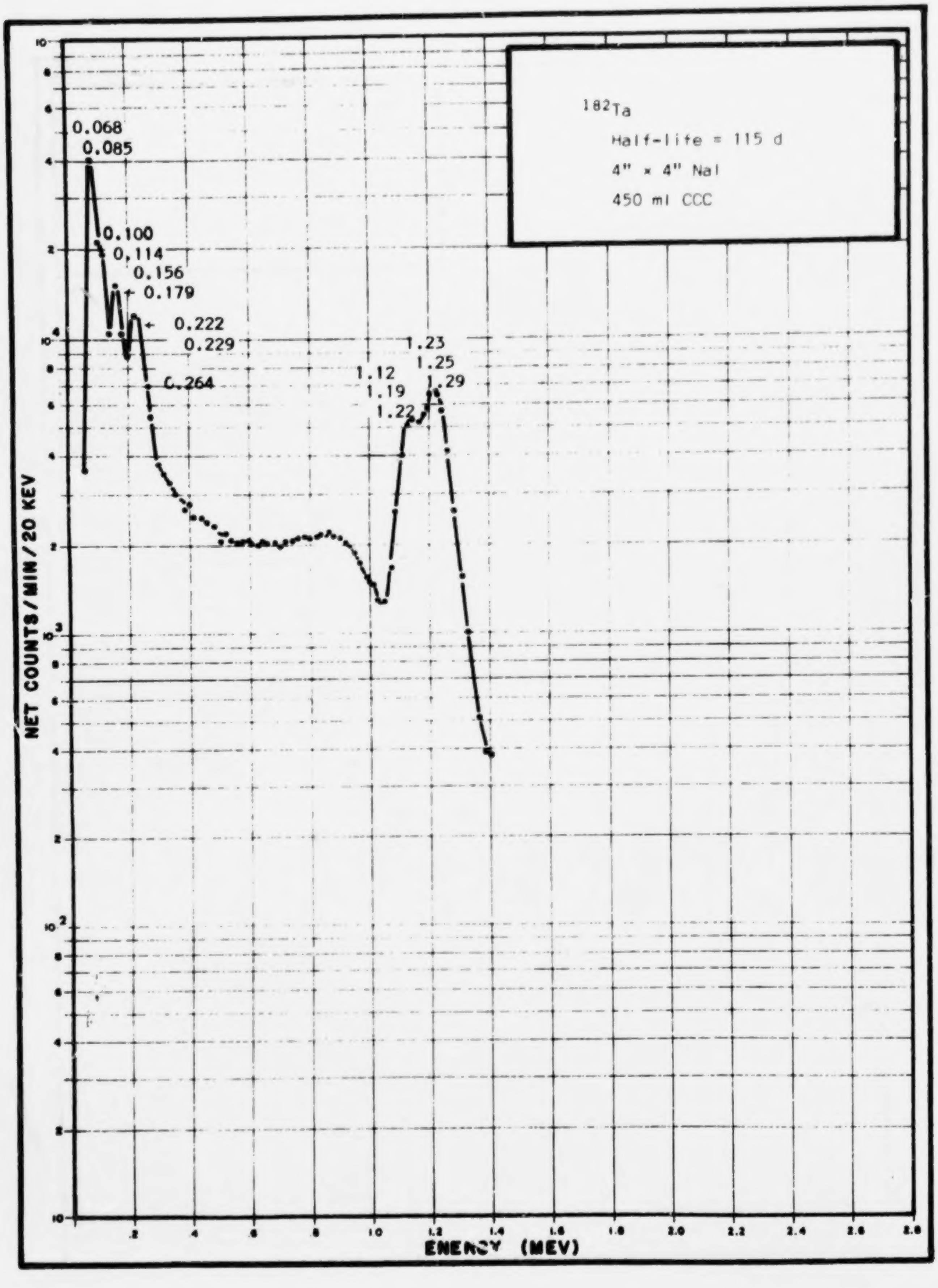


Figure 1.6-37 Gamma spectrum of ^{182}Ta - 450 ml

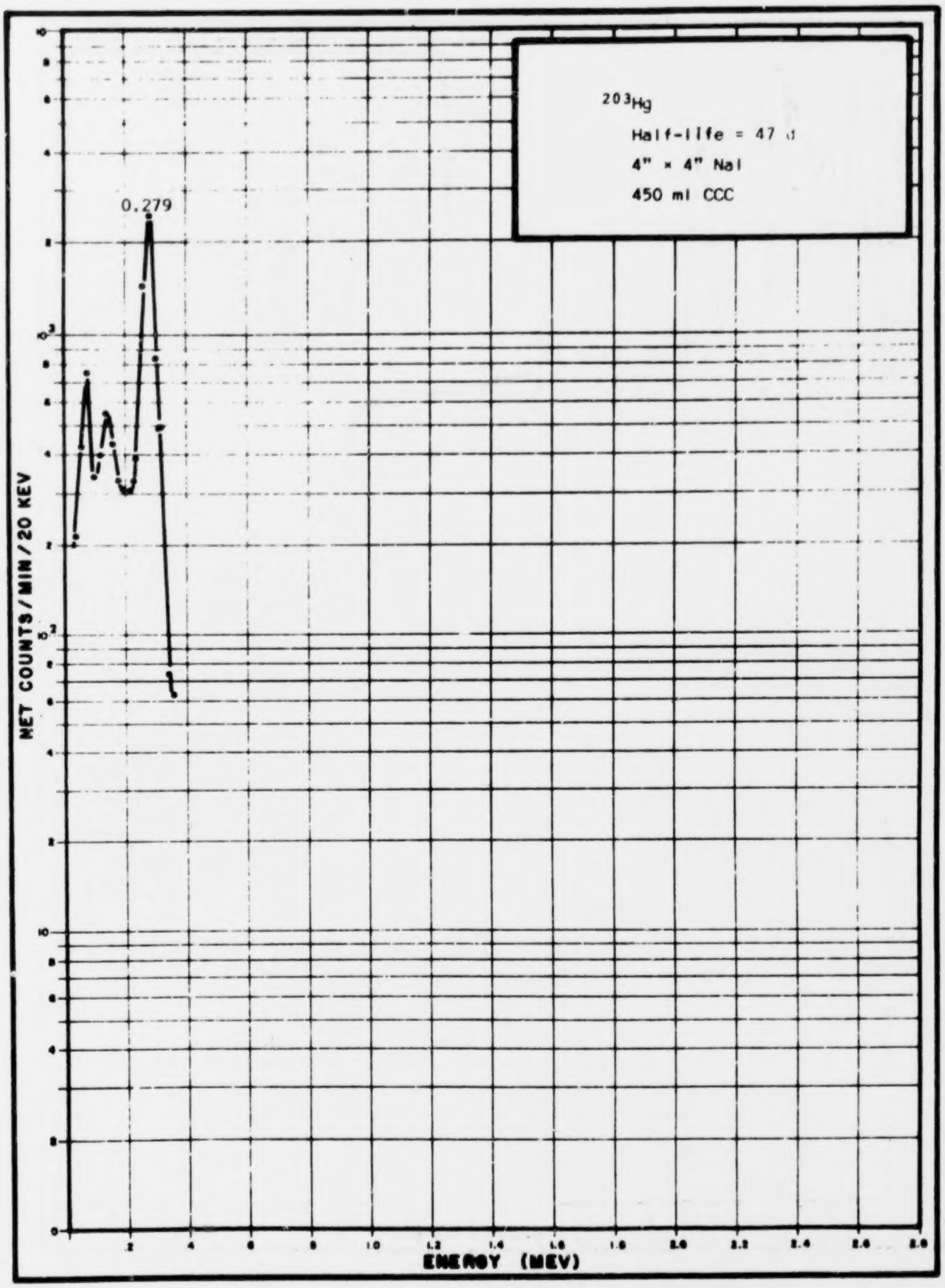


Figure 1.6-38 Gamma spectrum of ^{203}Hg - 450 ml

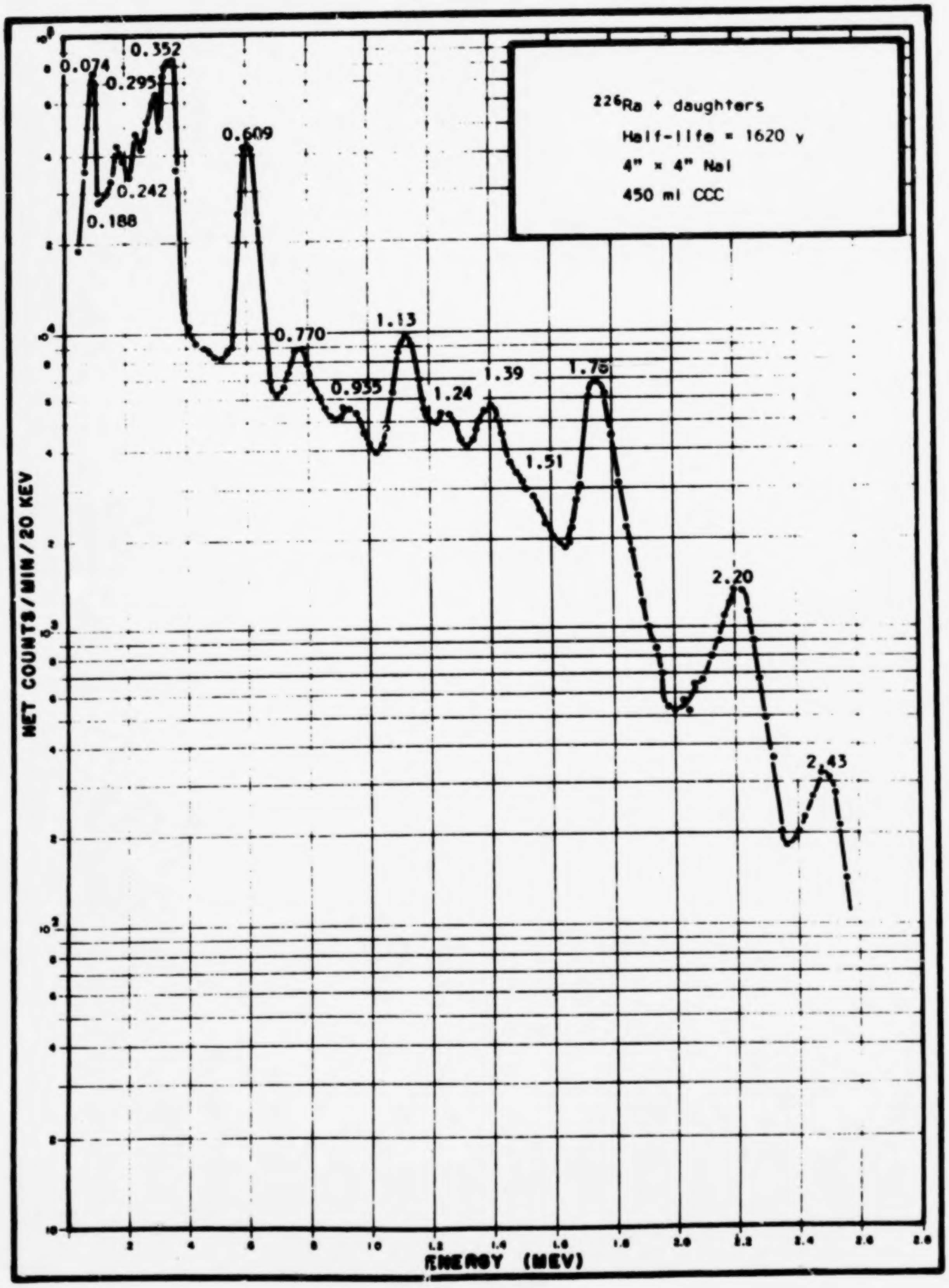


Figure 1.6-39 Gamma spectrum of ^{226}Ra and daughters - 450 ml

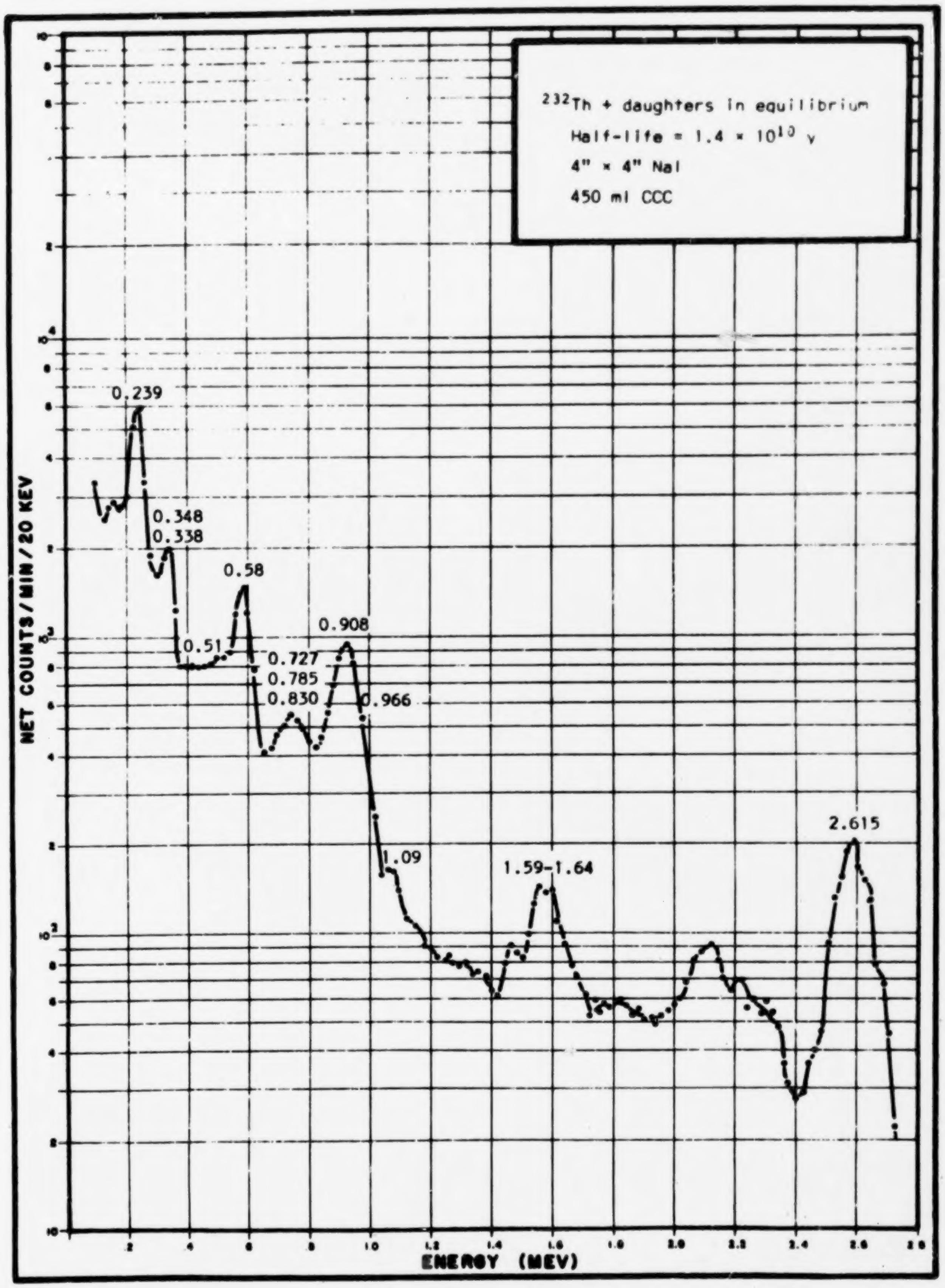


Figure 1.6-40 Gamma spectrum of ^{232}Th and daughters in equilibrium - 450 ml

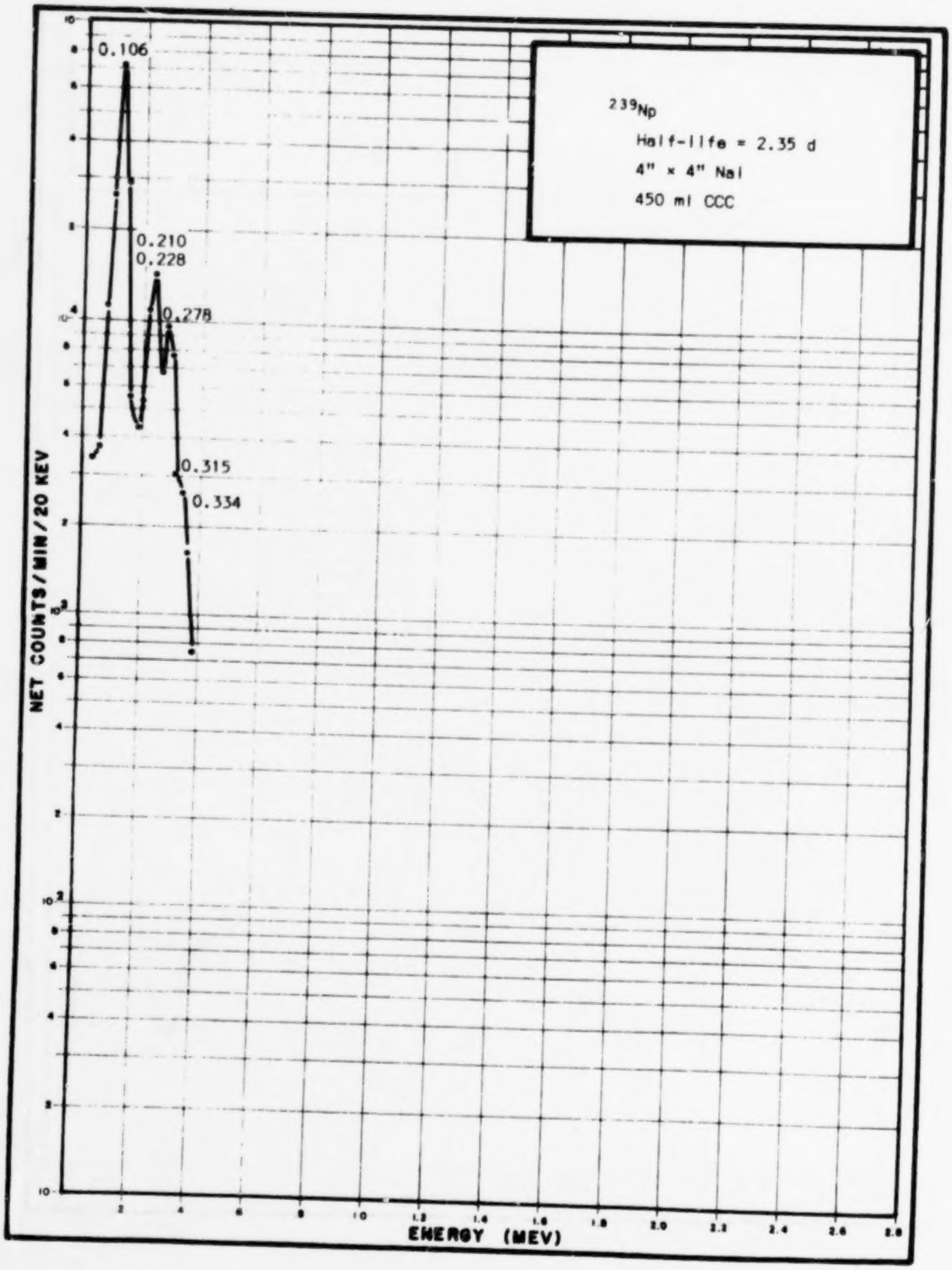


Figure 1.6-41 Gamma spectrum of ^{239}Np - 450 ml

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SECTION 2.

QUALITY CONTROL

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SECTION 2. QUALITY CONTROL

2.0 INTRODUCTION

Maintenance of a continuous stream of accurate data from several laboratories is, as one might expect, an extremely difficult and challenging task. Application of quality control principles to radiological health measurements can minimize the amount of disparity within and among laboratories to a considerable extent. This is done by isolating discrepancies in analytical results and taking appropriate action to remedy the causative factors. While quality control procedures can greatly assist in obtaining consistent data, they obviously cannot guarantee accuracy. For maintaining production of precise, unbiased data, quality control is a continuous task.

Accurate data, as defined for the purpose of this manual, are data that are both precise and unbiased. This is illustrated pictorially in Figure 2.0-1. Complete control over analytical measurements requires day-to-day control over instrumentation, chemical steps, and associated factors at each individual laboratory. The procedures outlined in this Section document the overall accuracy of laboratory data and help to uncover divergence in the overall results. The application of three allied but independent procedures has been found most useful and is described. The procedures are:

1) "Blind" duplicate analysis of actual surveillance samples within one laboratory. This procedure allows a laboratory to evaluate its internal precision or reproducibility.

2) Cross-check analysis of natural environmental samples among several laboratories. This intercomparison procedure allows a laboratory to determine its agreement with other laboratories doing similar work.

3) Special standard sample analysis. This procedure allows a laboratory to study its accuracy, *i.e.*, the agreement of its results with a known value.

Actual surveillance samples are those processed as part of the normal laboratory workload. Natural environmental samples are portions of a large sample taken in addition to the actual surveillance samples and distributed among several laboratories. Special standard samples are natural environmental samples or carefully simulated environmental samples which have been prepared to contain a known or accurately determined concentration of the nuclide under study.

The most effective means of conducting the cross-check and special standard analysis procedures, when several laboratories are involved, is through an independent referee group. When such a group is not available, a system among the laboratories can be devised easily. The special standard sample analysis can also be applied within a single laboratory, but extreme care must be taken to prepare the standard samples by an accurate means divorced from the analytical method being studied. Statistical concepts are applied in all three procedures so that firm conclusions can be made as to the validity of the analytical data.

The over-riding factor in a successful quality control program is the selection of criteria for acceptable and attainable accuracy. Through experimentation and experience, criteria are selected that reflect both the capabilities of the laboratory and the requirements necessary for surveillance data. This point can not be overly stressed, because improper criteria will lead to false conclusions and will waste time and effort. A second important factor is the selection of a sufficient number of samples to properly test whether the analytical data meet the established criteria. Both of these factors have been considered in the development of the procedures presented here. The accuracy criteria are a function of the particular analysis under study, and the number of samples taken are adequate for a statistical test without imposing an unacceptable additional workload.

Each of the three quality control procedures described in this manual supplies the observer with different but complementary information. For example, before a laboratory can participate satisfactorily in intercomparisons, it is necessary that internal consistency be established. However, even after agreement among laboratories is observed, it is necessary to document that the data are unbiased. Therefore, each of the three procedures is a necessary part of the mechanism for complete validation of analytical measurements.

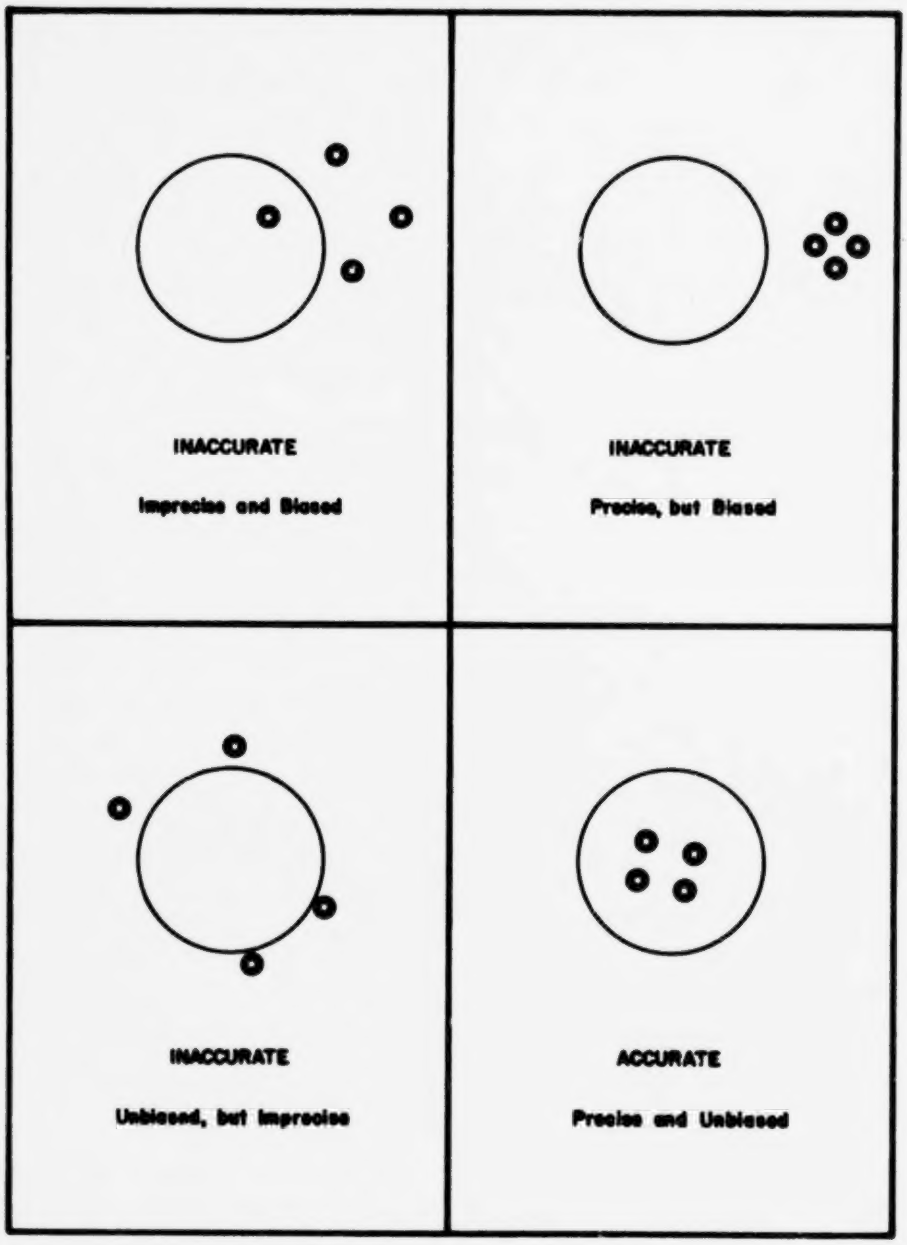
INACCURATE
Imprecise and Biased
INACCURATE
Precise, but Biased
INACCURATE
Unbiased, but Imprecise
ACCURATE
Precise and Unbiased

Figure 2.0-1 Precision, bias, and accuracy

2.1 INTERNAL REPRODUCIBILITY

One criterion of the validity of a laboratory's analytical results is its ability to reproduce measurements internally within acceptable limits. If a laboratory is unable to meet this test, any single result is questionable. A program of replicate measurements on a portion of the actual surveillance sample workload and the maintenance of appropriate records will demonstrate the reproducibility of data, or will quickly point out problem areas. This procedure will not indicate whether a constant bias is present in the measurements. However, when data are precise, systematic bias can be uncovered by another procedure (2.3).

For "blind" duplicate analysis, at least twenty actual surveillance samples are recycled randomly into the normal stream of analytical work. Twenty analyses in duplicate will supply sufficient data for the evaluation that is described here. The time required to collect data from twenty or more of these duplicated analyses depends on the workload involved for a particular type of analytical method. As a rough guide, approximately 20% of the analytical workload should be analyzed in duplicate. For example, if one hundred or more samples are processed each month and 20% are duplicated, a one-month data collection period is sufficient. On the other hand, if fifty samples are processed each month and 20% are duplicated, a two-month data collection period will be required to accumulate twenty duplicated analyses. Records are kept of appropriate data, such as the instrument used, the date of analysis, and the technician performing the analysis. Figure 2.1-1 is an example of a form suitable for a record of this kind.

One can calculate the mean range between duplicate analyses from the standard deviation of an analytical method, which is a function of the concentration of the nuclide under study. A standard deviation is assigned on the basis of experience with the analytical method and on a judgment that it represents satisfactory precision for the program considered, here a surveillance program. Once the mean range has been computed, permissible range limits for various degrees of probability can be readily calculated. Although the range distribution is slightly skewed, normal distribution statistics can be used to approximate the desired probability levels.(1)

Sample Number	ANALYSIS 1				ANALYSIS 2			
	Date	Counter	Analyst	Result	Date	Counter	Analyst	Result

Figure 2.1-1 Record of duplicate analyses

The probability levels are calculated as follows:

1) Select a standard deviation value σ for individual results obtained by the analytical method.

2) Using the factor d_2 from Table 2.1-1, find the mean range $\overline{R}$ from the relationship $\overline{R} = d_2\sigma$. Here d_2 is a function of the number of replicates involved, in this case, two. Table 2.1-1 is a standard statistical table used for calculating range control limits from standard deviation values, and includes this d_2 factor.

3) Using the factor D_4 from Table 2.1-1, calculate the upper range control limit $\overline{R} + 3\sigma_R$.

$$\overline{R} + 3\sigma_R = D_4\overline{R}$$

where σ_R is the standard deviation of the range distribution, and D_4 is a calculating factor for the upper control limit for ranges, which depends on the number of replicates involved, in this case, two.

4) Calculate the intermediate probability levels $\overline{R} + \sigma_R$ and $\overline{R} + 2\sigma_R$ from the mean range and the upper control limit as follows:

$$\overline{R} + \sigma_R = \overline{R} + \frac{1}{3}(D_4\overline{R} - \overline{R})$$

$$\overline{R} + 2\sigma_R = \overline{R} + \frac{2}{3}(D_4\overline{R} - \overline{R})$$

Table 2.1-2 gives a sample of these calculations, using the analysis of cesium 137 in milk as a specific example. The standard deviation of this analysis as performed in National Center for Radiological Health laboratories is 5 picocuries per liter (pCi/liter) when the cesium 137 concentration is less than or equal to 100 pCi/liter and is 5% when the cesium 137 concentration is greater than 100 pCi/liter. The values given in Table 2.1-2 are expressed in graphical form in Figure 2.1-2, yielding a control chart on which one can readily study whether observed ranges are within acceptable limits.

Table 2.1-1 Factors for computing mean range and range control limits

Number of Observations N	Factor for Mean Range d_2	Factors for Range Control Limits D_3	 D_4
2	1.128	0	3.267
3	1.693	0	2.575
4	2.059	0	2.282
5	2.326	0	2.115
6	2.534	0	2.004
7	2.704	0.076	1.924
8	2.847	0.136	1.864
9	2.970	0.184	1.816
10	3.078	0.223	1.777

Table 2.1-2 Sample calculation of range limits for internal duplicate analyses (^{137}Cs in milk)

Mean of Duplicate Analyses Concentration (pCi/liter)*	Standard Deviation σ	Mean Range $\overline{R} = d_2\sigma$ $d_2 = 1.128$	Upper Control Limit $\overline{R} + 3\sigma_R = D_4\overline{R}$ $D_4 = 3.267$	Intermediate Control Limits $\overline{R} + \sigma_R$ $= \overline{R} + \frac{1}{3}\left(D_4\overline{R} - \overline{R}\right)$ $= 1.755\ \overline{R}$	 $\overline{R} + 2\sigma_R$ $= \overline{R} + \frac{2}{3}\left(D_4\overline{R} - \overline{R}\right)$ $= 2.510\ \overline{R}$
≤ 100	5.0	5.6	18.3	9.8	14.1
150	5% 7.5	8.5	27.8	14.9	21.3
200	5% 10.0	11.5	36.9	19.8	28.4
250	5% 12.5	14.1	46.1	24.7	35.4

* 1 picocurie = 10^{-12} curie

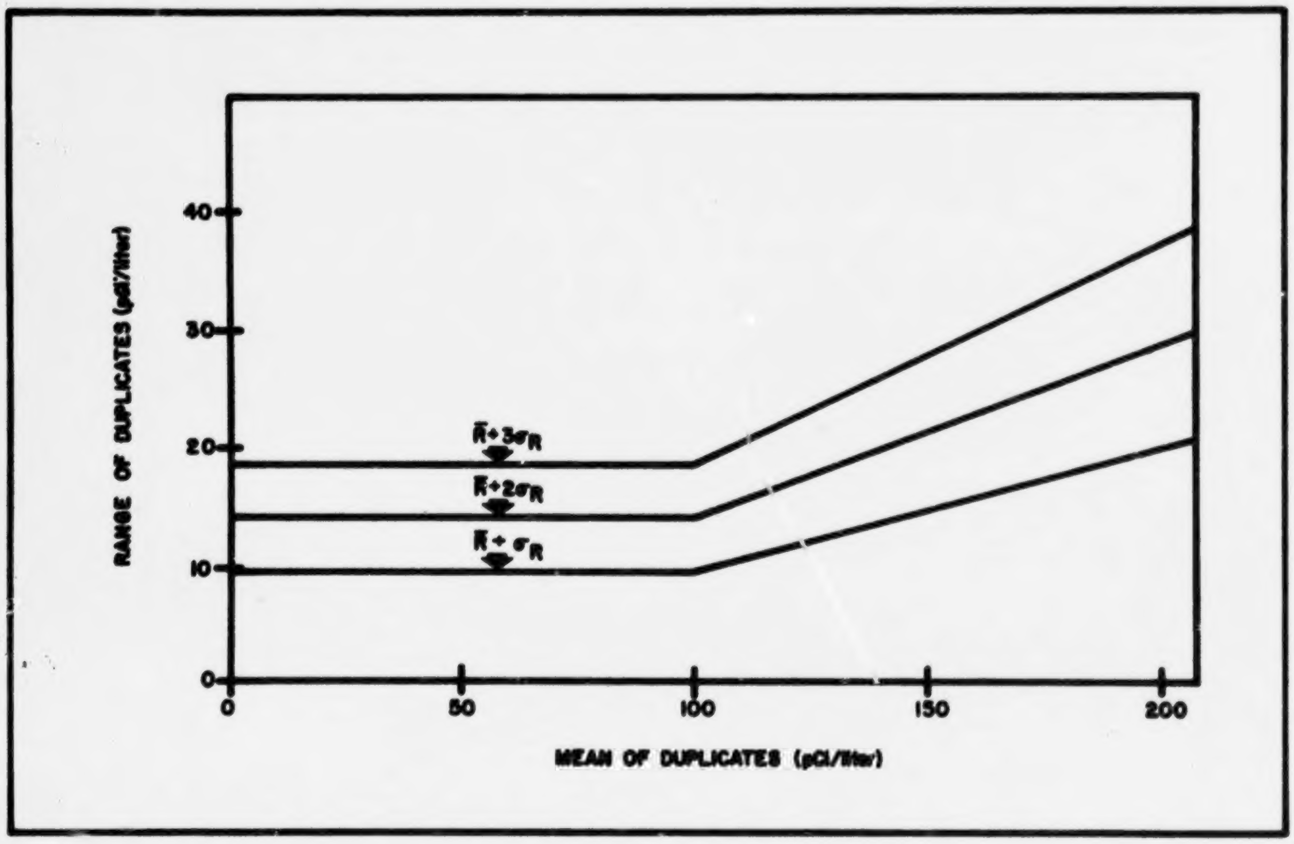

Figure 2.1-2 CONTROL CHART - Range probability levels for duplicate analyses (^{137}Cs in milk)

The observed range between data from duplicate analyses is evaluated as being $\leq (\overline{R} + \sigma_R)$, $\leq (\overline{R} + 2\sigma_R)$, $\leq (\overline{R} + 3\sigma_R)$, or $> (\overline{R} + 3\sigma_R)$, using the curves of Figure 2.1-2. After an appropriate period, when twenty or more duplicate sets have been accumulated, the degree to which a laboratory has met the desired limits can be determined. One way of doing this is to analyze the distribution of ranges in the $\leq (\overline{R} + \sigma_R)$, $\leq (\overline{R} + 2\sigma_R)$, $\leq (\overline{R} + 3\sigma_R)$, and $> (\overline{R} + 3\sigma_R)$ categories. Theoretically, 84% of the ranges should fall into the $\leq (\overline{R} + \sigma_R)$ category. This 84% consists of the 50% which should fall between zero range and $\overline{R}$, plus the 34% which should fall between $\overline{R}$ and $\overline{R} + \sigma_R$. Similarly, 97.5% of the ranges should fall into the $\leq (\overline{R} + 2\sigma_R)$ category, and approximately 100% should fall into the $\leq (\overline{R} + 3\sigma_R)$ category.

Table 2.1-3 summarizes this type of evaluation. Experience with the procedure will enable the analyst to determine when acceptable distributions are obtained. Three distributions can occur — acceptable, unacceptable, and outlier — as shown in the examples in Table 2.1-3 and discussed below.

1) An acceptable distribution will closely follow the expected distribution of ranges or will be shifted to the $\leq (\overline{R} + \sigma_R)$ and $\leq (\overline{R} + 2\sigma_R)$ categories, indicating better internal precision than expected.

2) An unacceptable distribution will be shifted to the $\leq (\overline{R} + 2\sigma_R)$, $\leq (\overline{R} + 3\sigma_R)$, and $> (\overline{R} + 3\sigma_R)$ categories, indicating a poorer precision than expected.

3) An outlier distribution will follow the expected distribution, but will have one or two results in the $> (\overline{R} + 3\sigma_R)$ category, indicating that generally the precision is acceptable, but occasional poor analytical results are being obtained.

This evaluation provides a basis for further study of the analytical procedure, if necessary. However, if examination of duplicate results indicates grossly unsatisfactory analytical data before twenty duplicate analyses have been performed, investigative and corrective action can be started immediately. For example, if the first five sets of duplicates fall into the $\le (\overline{R} + 3\sigma_R)$ and $> (\overline{R} + 3\sigma_R)$ categories, corrective action should be taken at once.

Table 2.1-3 Range distribution evaluation of duplicate determinations

Category	$\leq \overline{R} + \sigma_R$	$\leq \overline{R} + 2\sigma_R$	$\leq \overline{R} + 3\sigma_R$	$> \overline{R} + 3\sigma_R$
Expected %	84	97.5	100	0
Expected No.*	16.8	19.5 (16.8 + 2.7)	20 (19.5 + 0.5)	0
Example 1* ACCEPTABLE	15	20 (15 + 5)	20 (20 + 0)	0
Example 2* UNACCEPTABLE	9	15 (9 + 6)	17 (15 + 2)	3
Example 3* OUTLIER	16	19 (16 + 3)	19 (19 + 0)	1

* based on duplicate analyses of 20 samples

2.2 INTERLABORATORY INTERCOMPARISONS

When several laboratories are provided with portions of a homogeneous environmental sample, a comparison among the laboratories can be made. Such cross-check analyses can provide data for all pertinent nuclides in a medium at the same time, and corrective action can be taken as a result of the information obtained. These intercomparisons do not provide information on accuracy, but can indicate when a particular laboratory is in disagreement with others or when general agreement among laboratories is poor.

Periodically (monthly or bimonthly), each participating laboratory makes triplicate analyses for the appropriate nuclides in a natural environmental cross-check sample. Agreement among laboratories is then measured by comparing the observed range of the laboratory means with predetermined allowable ranges. Statistically, the range is almost as efficient a measurement of dispersion as the standard deviation when the number of results in a set is small.(2) When the number of participating laboratories is greater than ten, the procedure becomes less efficient.(3)

Using factors found in statistical tables, allowable ranges are calculated from assigned standard deviations for individual determinations. These ranges depend on the concentration of the nuclide, the number of replicates, and the number of laboratories involved. The allowable ranges define a level which 97.5% of the observed ranges should not exceed when analytical specifications are being met.

The allowable ranges are calculated as follows:

1) Select a standard deviation σ for individual determinations.
2) Determine the standard deviation for means σ_m for each nuclide by dividing the assigned standard deviation for individual values σ by the square root of the number of replicate determinations N.

$$\sigma_m = \frac{\sigma}{\sqrt{N}}$$

3) Using the above standard deviation for means, calculate the average range for means $\overline{R}$ as follows:

$$\overline{R} = d_2\sigma_m$$

where d_2 is a calculating factor (Table 2.1-1) for the mean range, which depends on the number of participating laboratories.

4) Next, calculate the allowable range as follows:

$$\text{Allowable Range} = D\,\overline{R}$$

where D is a calculating factor (Table 2.1-1) which depends on the number of participating laboratories and the desired level of statistical confidence. The two-sigma ($2\sigma_R$) control limit for range is used. The D factors are calculated as follows:

$$\text{Allowable Range} = D\overline{R} = \overline{R} + \frac{2}{3}\left(D_4\overline{R} - \overline{R}\right)$$

$$\therefore\ D = 0.33 + 0.67\,D_4$$

where D_4 is a calculating factor (Table 2.1-1) for the upper control limit for ranges which depends on the number of participants.

A chart can be prepared showing the allowable range of laboratory means. Ninety-seven and one-half percent of the results should fall between zero and this allowable range. In the chart, the allowable range is shown as a function of the concentration of the nuclide and the number of laboratories involved. An example of such a chart for analysis of cesium 137 in milk is given in Figure 2.2-1, and the calculations for obtaining the curves are given in Table 2.2-1.

In the final analysis, observed ranges that are greater than the allowable range indicate that the laboratories do not agree with each other within the standard deviation chosen as acceptable for individual determinations among laboratories. In some cases, the agreement may not be acceptable because one laboratory result is divergent, while in other cases, the overall spread among the laboratory results may be excessive. Table 2.2-2 gives examples of cross-check data, showing several possible situations.

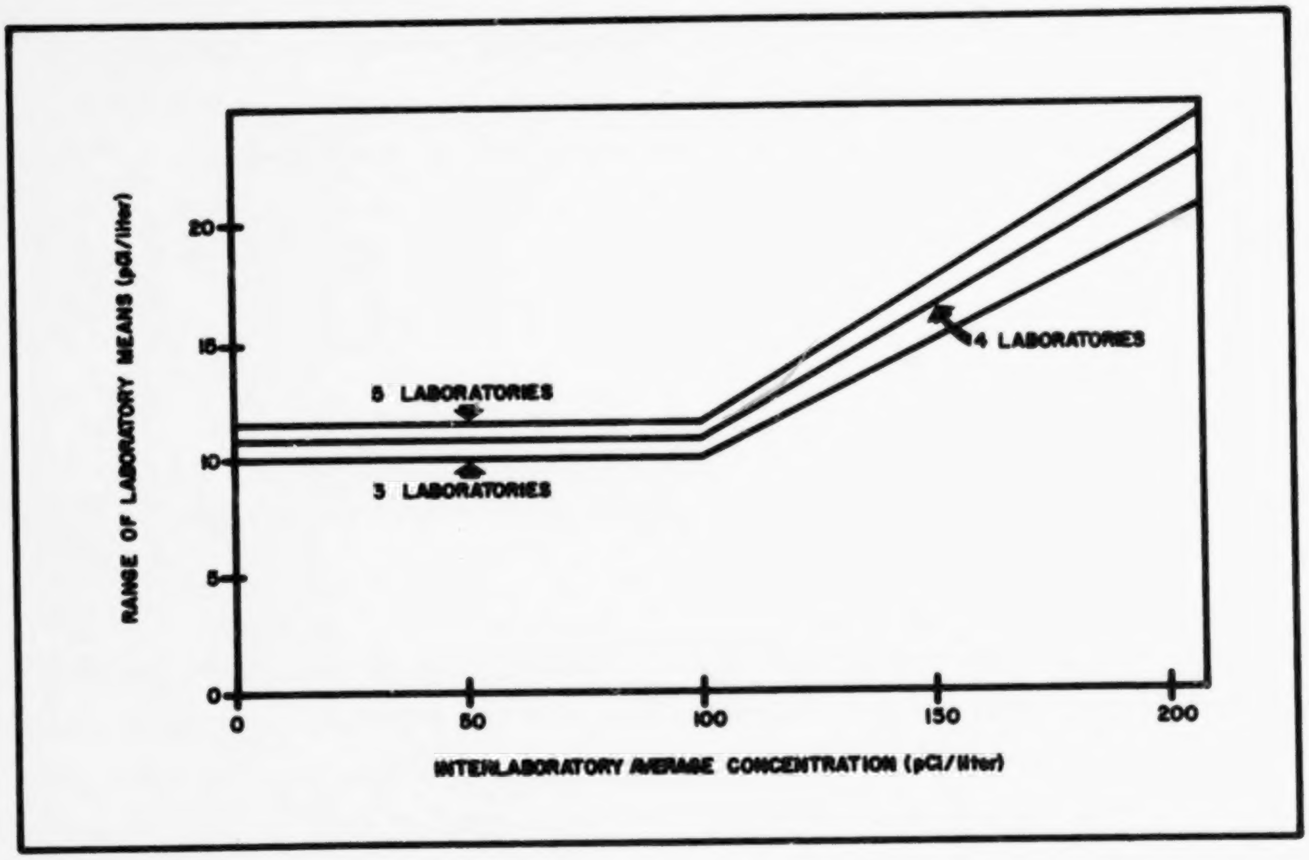

Figure 2.2-1 CONTROL CHART - Allowable ranges for interlaboratory intercomparisons (^{137}Cs in milk)

Table 2.2-1 Sample calculation of range limits for cross-check analyses among laboratories (^{137}Cs in milk)

Average of Laboratory Means	Standard Deviation	Standard Deviation	Mean Range ($\overline{R} = d_2\sigma_m$) and Allowable Range* ($D\overline{R} = \overline{R} + 2\sigma_R$)					
			Three Laboratories		Four Laboratories		Five Laboratories	
Concentration	Individual Determinations	Means	Mean Range	Allowable Range	Mean Range	Allowable Range	Mean Range	Allowable Range
(pCi/liter)	σ	σ_m $\sigma_m = \frac{\sigma}{\sqrt{N}}$ $N = 3$	$d_2 = 1.70$	$D = 2.05$ $D_4 = 2.57$	$d_2 = 2.06$	$D = 1.85$ $D_4 = 2.28$	$d_2 = 2.33$	$D = 1.74$ $D_4 = 2.11$
≤ 100	5.0	2.89	4.9	10.0	5.9	10.9	6.7	11.7
150	5% 7.5	4.34	7.4	15.2	8.9	16.5	10.1	17.6
200	5% 10.0	5.78	9.8	20.1	11.9	22.0	13.5	23.5
250	5% 12.5	7.23	12.3	25.2	14.8	27.4	16.8	29.2

* Allowable Range $= \overline{R} + 2\sigma_R = \overline{R} + \frac{2}{3}\left(D_4\overline{R} - \overline{R}\right) = D\overline{R}$, where $D = 0.33 + 0.67\,D_4$

Table 2.2-2 Evaluations of cross-check data (^{137}Cs in milk)

Laboratory Mean (pCi/liter)				Observed Range	Allowable Range	Observations
A	B	C	D			
6.7	8.0	0.5	3.7	7.5	10.9	ACCEPTABLE
255	239	250	248	16.0	27.2	ACCEPTABLE
14.3	5.7	0.6	10.3	13.7	10.9	UNACCEPTABLE General Disagreement
115	99	110	112	16.0	11.9	UNACCEPTABLE Laboratory B Divergent

2.3 LABORATORY ACCURACY

Analytical validity can be assured only when the data agree with a known true value. Natural or synthetic materials can be prepared to contain known concentrations of the nuclide(s) of interest and submitted for analysis. By statistically comparing the resulting data with the expected values, the degree of analytical validity of the results can be measured. However, this procedure is limited to studying only one or two nuclides in a particular medium at a time, and the samples must be carefully prepared to ensure that their nuclide concentration is well established. Control charts, so constructed as to determine the accuracy (precision and bias) of reported results, have been found very useful.

To apply this procedure, each participating laboratory must perform replicate analyses of special standard samples containing known concentrations (but unknown to the participants) of the nuclide(s) at one or more levels. The hypothesis tested by this procedure is that the reported analytical results could reasonably have been obtained from a normal population of analytical data whose mean is equal to a known value and whose standard deviation is equal to an assigned value.

From the data collected, two statistics are calculated: the mean of the replicate determinations, and the range of the determinations. The mean values, the range values, and the individual values are plotted on three types of control chart(4) which will be described.

2.3.1 Control Chart for Means (Mean Chart)

The control chart for means is a graphical presentation of a normal distribution which enables one to measure the amount by which the mean value of several individual determinations is biased from the true value. It is assumed that under satisfactory conditions the results from several laboratories will approximate a normal distribution. Therefore, failure of a mean value to fall within the limits established by the mean chart indicates that the analytical data are not from the expected normal distribution. Figure 2.3-1 is an example of a mean chart for analysis of cesium 137 in milk at a concentration of 460 pCi/liter. Explanations for the symbols used in the chart are given below.

1) The standard deviation for individual determinations σ is selected on the basis of past experience with the analytical method and a judgment as to the accuracy required.

2) The standard deviation for means σ_m is calculated by dividing σ by the square root of the number of individual determinations N. In the example, N equals four.

3) The known activity of the special standard sample is designated as the standard mean $\overline{X}$.

4) The upper and lower warning levels $\overline{X} \pm 2\sigma_m$ are the two sigma limits for the standard mean. Results which are acceptable should fall within the warning levels 95% of the time.

5) The upper and lower control limits $\overline{X} \pm 3\sigma_m$ are the three-sigma limits for the standard mean, and acceptable data should fall within the control limits 99.7% of the time.

For replicate determinations obtained by a laboratory, a mean value falling outside the warning levels indicates that a bias in the results may be present and that further information should be obtained. A result that falls outside the control limits indicates that the data are excessively biased and that corrective action should be taken.

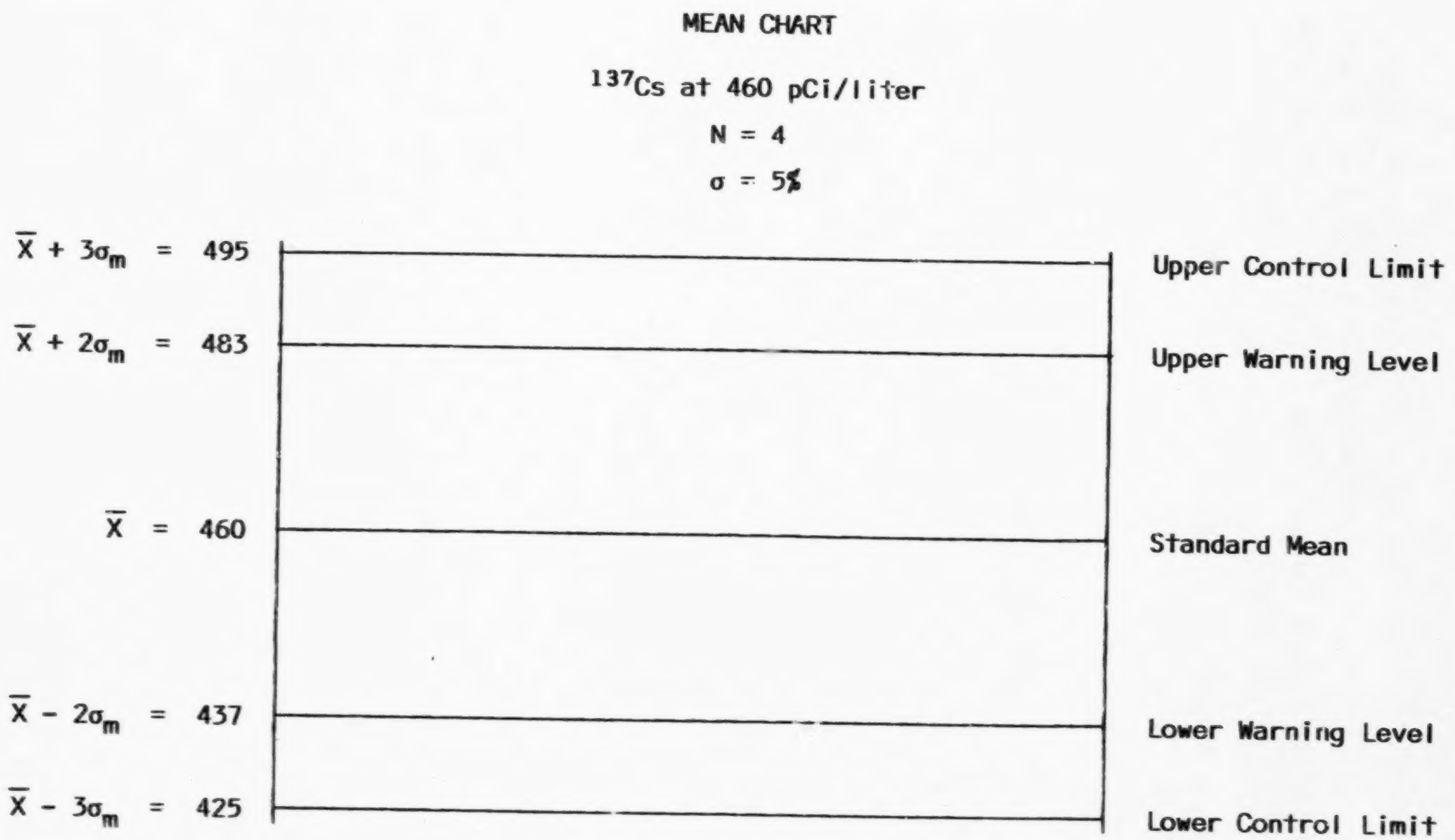

Figure 2.3-1 Example of control chart for means as applied in interlaboratory studies

2.3.2 Control Chart for Ranges (Range Chart)

The control chart for ranges is a graphical presentation of the distribution of ranges resulting from a normal population of individuals. Here, standard deviation values for the range, calculated from standard deviation values for individual determinations, are used to approximate the desired probability levels for ranges. Therefore, a range value which does not fall within the limits established on the range chart indicates that the analytical results are not from the expected normal distribution. Figure 2.3-2 is an example of a range chart for analysis of cesium 137 in milk at a level of 460 pCi/liter. Explanations for the symbols in the range chart are given below.

1) The same standard deviation value σ for individual determinations selected for the mean chart can be used for the range chart, but this is not always necessary. Different standard deviation values for the two charts can be used since the mean chart deals with bias and the range chart with internal precision. The desired standards for the two may be different.

2) The mean range $\overline{R}$, which is the average range that would be observed if a very large number of range determinations were made under ideal conditions, is analogous to the standard mean in the mean chart.

3) The factors d_2, D_3, D_2, and D_4 are taken or calculated from Table 2.1-1 and yield the upper warning level, upper control limit, and lower limit for ranges. These factors are a function of the number of replicate determinations. For four determinations they are:

$d_2 = 2.06$
$D_3 = 0.00$
$D_2 = 1.84$
$D_4 = 2.28$

4) The lower limit for ranges is zero. Because the replicate determinations are independently obtained, values falling consistently below the mean range indicate that the observed internal precision is better than expected.

The range chart is analogous to the mean chart. Thus, a range value which exceeds the upper warning level indicates questionable precision and the need for further study. Likewise, a range value which exceeds the upper control limit indicates unsatisfactory precision and the need for corrective action.

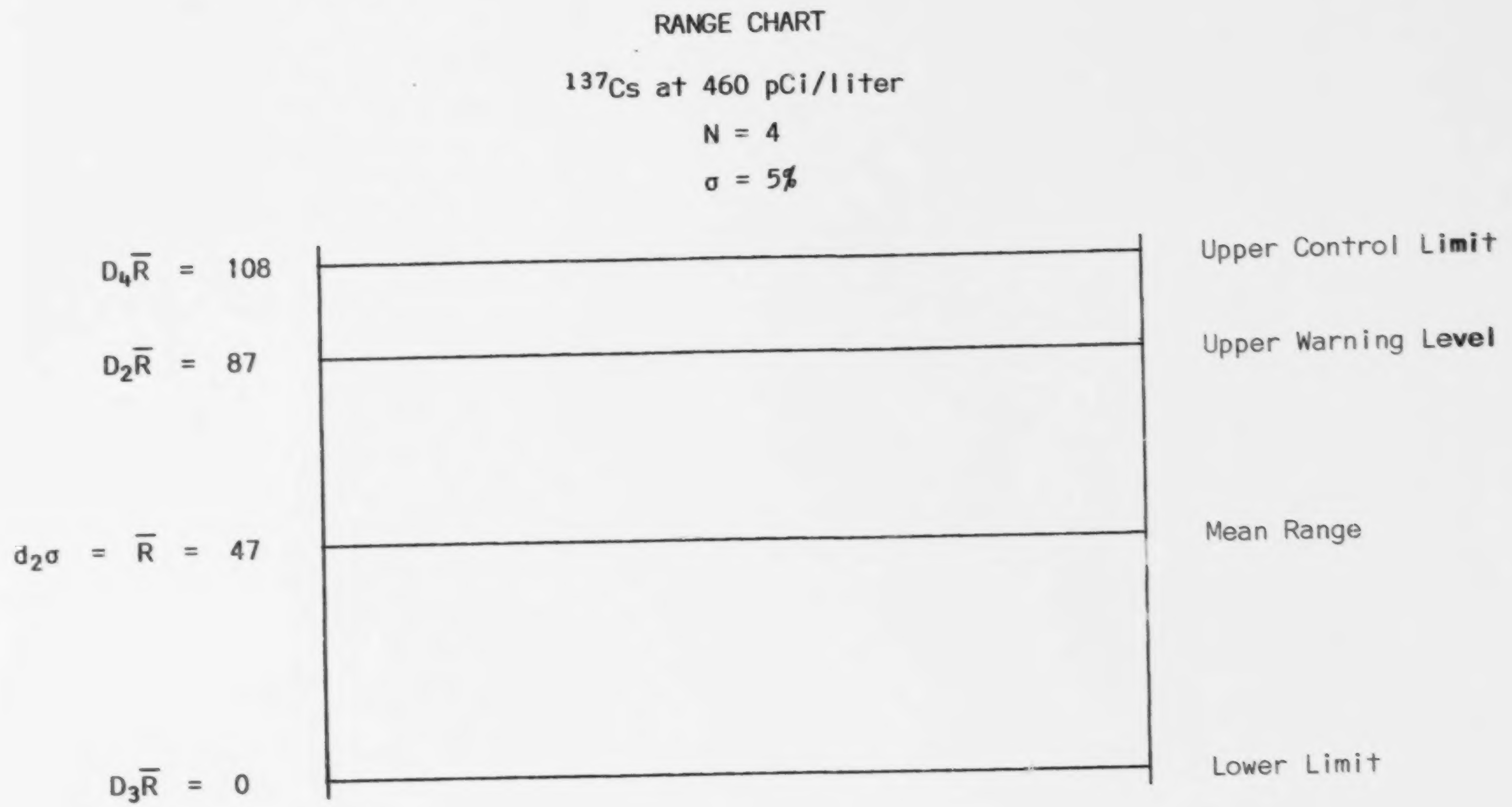

Figure 2.3-2 Example of control chart for ranges as applied in interlaboratory studies

2.3.3 Control Chart for Individual Determinations (Individual Chart)

The control chart for individual determinations is similar to the mean chart. For the individual chart, each individual value is utilized instead of the mean value. In various ways, the individual chart can indicate specific causes for discrepancies in laboratory data. For example, if the mean value for a laboratory is high, plotting the individual data separately for each instrument used may show whether all the individual results are high, indicating a general problem, or whether the results from one instrument are in question.

An example of the application of the individual chart for analysis of cesium 137 in milk at the 460 pCi/liter level is shown in Figure 2.3-3. The individual chart is constructed in the same manner as the mean chart except that the standard deviation for individual results σ is used instead of the standard deviation for means σ_m. The central value on this chart X is numerically equal to the known concentration in the special standard sample. From these parameters (X and σ), the upper and lower warning levels $X \pm 2\sigma$ and the upper and lower control limits $X \pm 3\sigma$ are obtained. The data are evaluated as in the mean and range charts.

While the procedure of special standard sample analysis has been described in terms of studying several laboratories, it is very useful even in a single laboratory. By preparing a standard sample, periodically analyzing this sample in replicate, and keeping a running chart of the data, a laboratory can monitor its own accuracy. However, it is best applied to several laboratories when an external group, such as the Analytical Quality Control Service of the National Center for Radiological Health, conducts such experiments on an autonomous basis.

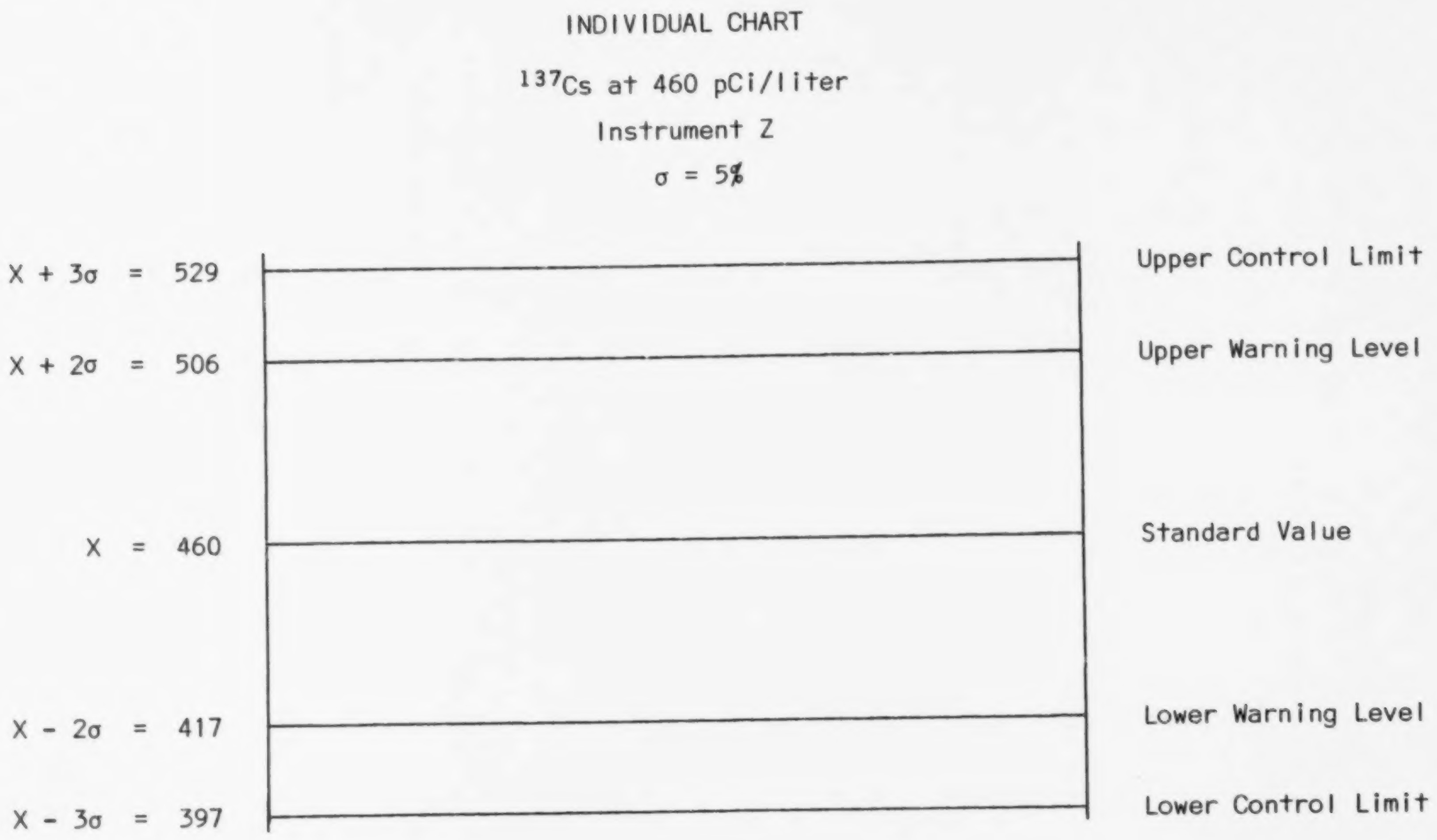

Figure 2.3-3 Example of control chart for individual determinations as applied in interlaboratory studies

2.4 SUMMARY

The primary goal of an analytical quality control program — that of maintaining analytical validity — can be attained by constant application of the control chart technique. The internal precision of a laboratory's data is determined through application of the control chart for ranges. The bias from a known value is readily detected by application of the control chart for means. Application of the control chart for individual determinations to unacceptable data provides the analyst with information on which to base recommendations for corrective measures. Applied together in a continuous program of quality control, the three control charts permit detection of unacceptable data both within and among laboratories, and indicate appropriate remedial action.

The National Center for Radiological Health, through its Analytical Quality Control Service instituted in 1962, has effectively applied the control chart technique to analyses performed in its laboratories for strontium 90, iodine 131, cesium 137, potassium 40, radium 226, and stable calcium in a variety of environmental samples. The technique can be used to study any other analysis of environmental samples as long as a special standard sample can be prepared to contain a known amount of the nuclide or element of interest and an acceptable and attainable level of accuracy can be selected.(5)

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SECTION 3.

MILK

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SECTION 3. MILK

3.0 INTRODUCTION

This section includes methods currently used for radiochemical and related stable chemical analyses of liquid milk at laboratories of the National Center for Radiological Health. Radiochemical analyses include those for strontium 89, strontium 90, and barium 140. Stable chemical analyses include those for determining strontium carrier recovery, calcium, and potassium.

All of the Center's laboratories use the REFERENCE METHOD — TBP Extraction for the determination of strontium 90 in liquid milk to aid in maintaining interlaboratory quality control and as an intralaboratory check for routine procedures. The method should not be attempted by untrained technicians.

The TCA PRECIPITATION METHOD — Nitric Acid Separation is applicable to the analysis of any liquid milk sample for strontium 89 and strontium 90 and is designed for mass analyses.

The ION-EXCHANGE PROCEDURE — TBP Extraction is applicable to the analysis of strontium 89, strontium 90, and barium 140 in homogeneous liquid milk samples, whereas the BATCH ION-EXCHANGE PROCEDURE or the methods for ashed milk samples should be used for analyses of these radionuclides in non-homogeneous samples. The ion-exchange procedures are designed for analyses of large numbers of samples and can be applied to milk containing fresh fission products as well as milk containing only long-lived fission products.

The recovery of strontium carrier, which is an integral part of all the radiochemical procedures for the determination of radiostrontium, can be determined by tracer, gravimetric, or flame photometric methods. The FLAME PHOTOMETRIC METHOD can be adapted to all of the procedures previously mentioned.

The REFERENCE METHOD (Overman) is the accepted standard method for the determination of calcium at all of the Center's laboratories and is used to maintain interlaboratory quality control. The PERMANGANATE TITRATION method for the determination of calcium is similar to the REFERENCE METHOD, except that the solution analyzed for calcuim is obtained by ion-exchange separation. The EDTA TITRATION method for calcium is rapid. However, the endpoint of the titration is difficult to determine, and a correction factor must be applied because the method yields results which have a high bias.

The FLAME PHOTOMETRIC METHOD for potassium is used as a comparison for determinations made by GAMMA SPECTROMETRY.

The choice of methods for radiochemical and stable chemical analyses should be based on the individual laboratory's needs and capabilities. Precision needed in analyses, skill of technicians, and availability of equipment and materials should always be considered in selecting one method above another.

3.1 PREPARATION OF SAMPLES

3.1.1 Preservation

To avoid spoilage, precautions are taken in the handling, shipping, and storing of milk samples. Immediately after the collection of a milk sample, a preservative, such as merthiolate or formaldehyde (~3 ml 37% formaldehyde solution per liter of milk), is added to the sample and, if possible, the sample is refrigerated.

3.1.2 Ashing

Ashing of milk is not necessary for most of the analytical procedures in this section. However, when ashed milk is required the following technique for ashing liquid milk is used.

Apparatus

analytical oven
Corning Ware dish
muffle furnace

Procedure

1. Transfer an aliquot of the milk sample to tared Corning Ware dishes.
2. Dry in oven at 100° C for 48 hours.
3. Transfer the sample to a muffle furnace, and raise the temperature slowly to 550° C. Ash at 550° C for 24 hours.
4. Cool, weigh, and grind the ash to a fine powder.
5. Analyze the milk ash by appropriate procedures given in SECTION 4. FOOD, parts 4.2 and 4.3.

3.2 DETERMINATION OF RADIOACTIVITY

3.2.1 Strontium 90

REFERENCE METHOD — TBP Extraction

To maintain accuracy at all National Center for Radiological Health laboratories, a reference method for determining strontium 90 in milk is used periodically to check the routine analytical procedures. This method is also used to analyze samples requiring a high degree of accuracy. It does not have the virtues of a routine procedure such as rapidity, adaptability for multiple analysis, and use by untrained technicians. Operation in the routine laboratory is limited by the use of strontium 85 tracer. In view of these differences, the procedure cannot be considered applicable to routine analysis of strontium 90 in environmental samples.

Principle of Method

Strontium carrier and strontium 85 tracer are first added to a 1-liter sample of milk to enable measurement of chemical recovery. Milk proteins, constituting the bulk of interfering solids, are removed by an initial precipitation with trichloroacetic acid. Sample volume is reduced by a basic carbonate precipitation. Strontium is extracted as the nitrate along with alkaline earths and lead, and washed with concentrated nitric acid. Any residual yttrium 90 daughter of strontium 90 is removed by hydroxide precipitation. Stable yttrium carrier is added to the solution to enable measurement of yttrium recovery, and the solution is stored to allow yttrium 90 to grow in.

After a suitable ingrowth period, yttrium is separated from strontium (and barium, radium, and lead) by hydroxide precipitation. The yttrium hydroxide is dissolved in nitric acid, from which yttrium is extracted into tributyl phosphate to separate it from any contaminating lanthanum 140. Yttrium is then re-extracted into dilute acid. It is precipitated as the oxalate and counted in a low-background beta counter. After being counted, the oxalate precipitate is ashed, and the yttrium oxide is weighed to determine yttrium recovery.

The supernatant solution remaining from the yttrium hydroxide precipitation is counted for the gamma activity of strontium 85. This activity is compared with that of an equivalent aliquot of the strontium 85 tracer solution to determine strontium recovery.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N), 6N
carrier solutions:
  Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$: 5 mg Fe^{+3} per ml
  Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 88 mg Sr^{+2} per ml
  Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml
ethyl alcohol, C_2H_5OH: 95%
hydrochloric acid, HCl: 6N, 3N, 2N
nitric acid, HNO_3: fuming (90%), concentrated (16N), 14N, 8N, 1N, 0.1N
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N
phenolphthalein indicator, $C_{20}H_{14}O_4$: 1% w/v
sodium carbonate, Na_2CO_3: 3N
sodium hydroxide, NaOH: 6N
strontium 85 tracer: $\sim 3 \times 10^4$ cpm ^{85}Sr per ml, standardized at time of sample count
tri-*n*-butyl phosphate [TBP], $(C_4H_9)_3PO_4$: pre-equilibrated with 14N HNO_3
trichloroacetic acid [TCA], CCl_3COOH: 50% w/v, 5% w/v

Apparatus

analytical balance
analytical oven
Buchner funnel, Coors No. 3
desiccator
glass counting vial, 8-dram capacity, with cap
glass fiber filter, 2.4-cm diameter
magnetic stirrer, with stirring bars
Millipore Type OH membrane filter, 2.5-cm diameter
pH meter
suction-filtration apparatus (Millipore Pyrex Hydrosol Microanalysis Filter Holder or equivalent)

Procedure

PROCESS ALL SAMPLES IN TRIPLICATE.

1. Pipette 1.0 ml of strontium 85 tracer into each of three 100-ml volumetric flasks to be used for recovery measurement. Add 1 ml of 6N HCl and 1 ml of strontium carrier, and bring the volume to 100 ml with distilled water. Store until time for sample counting (Step 36).
2. Using the same pipette as in Step 1, add 1.0 ml of strontium 85 tracer to each of three 1-liter replicates of milk at room temperature. Using another pipette, add 1 ml of strontium carrier to the milk, and mix thoroughly.
3. Add 300 ml of 50% TCA solution, stir thoroughly, and allow to stand for 30 minutes, mixing occasionally.
4. Filter through Whatman No. 42 filter paper, using a Buchner funnel. When almost dry, press down firmly on the curd with a flat-surfaced instrument, such as the bottom of a flask, to improve recovery.
5. Transfer the curd to a beaker. Add 350 ml of 5% TCA, and mix thoroughly with a beater until curd and paper are reduced to pulp. Then filter as in Step 4.
6. Repeat Step 5; discard residue.
7. Combine the filtrates in a 3-liter beaker, and adjust the pH to 7-8 with 6N NaOH, using phenolphthalein as indicator. The pH is not critical.
8. Add 50 ml of 3N Na_2CO_3, mix thoroughly, and allow to stand for at least 4 hours, but preferably overnight, to let the precipitate settle.
9. Siphon off the supernate and discard it. Transfer the precipitate with the remaining supernate to a 250-ml glass centrifuge bottle. Centrifuge, and discard the supernate.
10. Wash the beaker from Step 9 with approximately 100 ml of distilled water in several portions. Transfer the water to the centrifuge bottle containing the precipitate. Stir, centrifuge, and discard the supernate.
11. Dissolve the precipitate in 10 ml of 8N HNO_3, and transfer the solution to a 250-ml beaker. Evaporate almost to dryness in a hot water bath.

12. Add 10 ml of fuming HNO_3 and 20 ml of concentrated HNO_3 to give approximately a 75% HNO_3 solution. Let stand at room temperature for 15 minutes, stirring occasionally, to develop the precipitate.
13. Filter with suction through a glass fiber filter using a Millipore filter apparatus. Transfer the precipitate to the filtering funnel and wash the beaker three times with 10-ml portions of 75% HNO_3 pouring the wash through the filter funnel. Discard the filtrate.
14. Carefully disassemble the filtering apparatus. Using forceps, transfer the filter and precipitate to a 40-ml centrifuge tube, dissolving the precipitate into the tube with minimal portions of distilled water. Rinse the filtering chimney with minimal portions of distilled water, collecting the rinse in the same centrifuge tube. Keep the total volume to less than 15 ml.
15. Add 1 ml of iron carrier, and stir thoroughly. Adjust the pH to 5-6 by adding a few drops of concentrated NH_4OH. Check pH with universal pH paper. Digest the hydroxide precipitate in a hot water bath for 10 minutes. Stir occasionally.
16. Centrifuge, and decant the supernate into another 40-ml centrifuge tube. RECORD THE TIME OF DECANTATION AS THE BEGINNING OF YTTRIUM 90 INGROWTH.
17. Wash the ferric hydroxide precipitate with 10 ml of distilled water. Centrifuge, and combine the supernate with that from Step 16. Discard the precipitate.
18. Add 1 ml 1N HNO_3 and 1.0 ml of yttrium carrier. Store the solution for 2 weeks for yttrium 90 to grow in.
19. On completion of the ingrowth period, precipitate the yttrium by dropwise addition of concentrated NH_4OH to the phenolphthalein endpoint. Centrifuge, and decant the supernate into a 100-ml volumetric flask. RECORD THE TIME OF DECANTATION AS THE END OF YTTRIUM 90 INGROWTH AND THE BEGINNING OF YTTRIUM 90 DECAY.
20. Dissolve the yttrium precipitate in 20 ml 0.1N HNO_3. Add concentrated NH_4OH dropwise to the phenolphthalein endpoint. Centrifuge, and decant the supernate into the volumetric flask from Step 19.
21. Repeat Step 20.
22. Acidify the combined solutions from Steps 19-21 by adding a few

milliliters of 2N HCl to the volumetric flask. Dilute to volume with distilled water. Set the solution aside until Step 36.

23. Dissolve the yttrium hydroxide precipitate from Step 21 in 5 ml of 14N HNO_3. Transfer the solution to a 60-ml separatory funnel; wash the tube with an additional 10 ml of 14N HNO_3 in small portions to complete the transfer.
24. Add 15 ml of TBP, and shake for approximately 5 minutes to equilibrate the two phases. Let the phases separate, and then draw off and discard the acid phase.
25. Add 15 ml of 14N HNO_3 to the separatory funnel, and shake for approximately 2-3 minutes. Allow phases to separate. Drain off the acid phase and discard it.
26. Repeat Step 25.
27. Extract yttrium from the organic phase by adding 10 ml of distilled water and shaking approximately 2-3 minutes. Allow phases to separate, and drain the aqueous phase into a 100-ml beaker.
28. Repeat Step 27 using 10 ml of 0.1N HNO_3 instead of distilled water, and drain the acid phase into the same 100-ml beaker as in Step 27.
29. Repeat Step 28.
30. To precipitate yttrium oxalate, add 5 ml of 2N oxalic acid to the solution in the beaker, and using a pH meter, adjust to pH 1.5 with 6N NH_4OH. [A magnetic stirrer is convenient for this step.] Digest for 30 minutes in a water bath at 80-90° C.
31. Place a 2.5-cm diameter membrane filter in the Millipore filtering apparatus. Transfer the solution containing the yttrium oxalate precipitate to the filtering chimney, and apply suction. Wash the beaker with three 10-ml portions of warm distilled water, and pour through the filter. Further wash the precipitate with three 10-ml portions of 95% alcohol. Discontinue suction, and remove the filter chimney. Allow the sample to dry in air for about two minutes.
32. Transfer the membrane filter containing the oxalate precipitate to an appropriate sample mount.
33. Count the beta activity of yttrium oxalate in a low-background beta counter. To confirm the absence of contamination by other radio nuclides, count the sample again after three weeks when the yttrium 90 activity has decayed to 0.4 percent of the initial activity.

34. Disassemble the sample mount, and transfer the filter with precipitate to a 15-ml crucible which has been fired and weighed. Heat slowly until the membrane filter is charred. Then ash in a muffle furnace for one hour at 800-900° C. Cool crucible in an oven at 110° C for one hour. Then cool to room temperature in a desiccator.

35. Weigh the ash as yttrium oxide [Y_2O_3], and calculate the yttrium recovery.

36. Pipette three 25-ml aliquots of the solutions from Steps 1 and 22 into 8-dram glass vials, and seal the tops.

37. Count the strontium 85 gamma activity of each vial three times in the same well crystal, and in more than one counting system, if available. Calculate the average count rate for each sample. Calculate strontium recovery by comparing average count rate of the original strontium 85 solution (Step 1) to that of the supernatant solution (Step 22).

    [Note: If a well crystal is not available, the samples can be prepared in plastic containers and counted on a solid crystal detector.]

Calculation

$$\text{strontium 90 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F \times G}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of strontium carrier by strontium 85 tracer

C = recovery of yttrium carrier

D = counting efficiency for yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

E = sample volume (liters)

F = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from the decantation of the yttrium 90 supernate [Step 19] to the time of counting

G = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t

is the time from the start of the ingrowth period [Step 16] until the time of decantation of the yttrium 90 supernate [Step 19]

3.2.2 Strontium 89 and Strontium 90

TCA PRECIPITATION METHOD – Nitric Acid Separation

This procedure is used to determine strontium 89 and strontium 90 in both homogeneous and non-homogeneous milk. It effectively removes fresh fission products from the strontium and yttrium residues even when the milk sample contains radioiodine and other fission products in excess of 10^6 picocuries per liter.

Analysis of approximately 20,000 samples by this method has shown that five technicians working together can analyze approximately 250 samples per month.

The method is not suitable for laboratories where relative humidity is high since the sample is counted as strontium nitrate in a stainless steel planchet. If the air is humid, the sample may pick up moisture to form nitric acid which can corrode the counting chamber and the planchet. Other sample mounting procedures, such as the nylon ring and disk, would overcome this.

Principle of Method

After addition of strontium carrier, the milk proteins are precipitated with trichloroacetic acid, and removed by filtration. Excess oxalic acid is added to the filtrate and the alkaline earths are precipitated as oxalates. The oxalates are then converted to nitrates to allow separation of calcium from strontium by differences in solubility. Strontium is scavenged with barium, iron, and rare earth carriers, after which yttrium 90 is removed by nitric acid extraction. The purified strontium nitrate precipitate is stored for one to two weeks to allow yttrium 90 to grow in.

The strontium nitrate is then dissolved and reprecipitated with 80% nitric acid, leaving yttrium 90 in the supernatant solution. Both fractions are placed in planchets and counted for beta activity. The strontium 89 activity is the calculated difference between the activity of total radiostrontium and that of strontium 90 (as yttrium 90).

Reagents

acetic acid, CH_3COOH: 1.5N
ammonium acetate, $NH_4C_2H_3O_2$: 3N
ammonium acetate buffer: pH 5.0
ammonium hydroxide, NH_4OH: concentrated (15N), 6N, 1N
ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 0.5% w/v
bromcresol green: 0.1% w/v in ethyl alcohol
carrier solutions:
  Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 7 mg Ba^{+2} per ml
  Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 16 mg Sr^{+2} per ml
hydrochloric acid, HCl: concentrated (12N), 0.5N
nitric acid, HNO_3: fuming (90%), concentrated (16N), 3N, 0.5N
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: saturated at room temperature
scavenger solution: 20 mg Fe^{+3} per ml, and 10 mg each Ce^{+3} and Zr^{+4} per ml
  Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$
  Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$
  Zr^{+4} as zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$
sodium chromate, Na_2CrO_4: 1N
trichloroacetic acid [TCA], CCl_3COOH: 50% w/v, 5% w/v

Apparatus

low-background beta counter
medium-porosity filter stick

Procedure

1. Pipette 100-ml aliquots of the sample into each of two porcelain evaporating dishes. Analyze these aliquots for calcium by the REFERENCE METHOD (Overman). (See 3.3.2, page 3-46.)
2. Transfer a 1-liter aliquot into a 2-liter beaker. Add 5.0 ml of strontium carrier solution (approximately 80 mg Sr^{+2}), and stir thoroughly.
3. Add 300 ml 50% TCA solution, and stir thoroughly to precipitate protein. Filter through Whatman No. 12 fluted filter paper, or Whatman No. 22 filter paper in a Buchner funnel, and collect the filtrate in a 3-liter flask. Wash the protein precipitate with 200 ml 5% TCA solution, and discard the precipitate.

4. Transfer the filtrate to a 2-liter beaker, rinsing the flask with 5% TCA solution. Add 125 ml saturated oxalic acid solution, and mix thoroughly. Adjust the pH to 3.0 with concentrated NH_4OH, using a standardized pH meter. Allow the alkaline earth oxalate precipitate to settle for 5 to 6 hours.
5. Aspirate the supernate through a medium-porosity filter stick. Wash the beaker and the precipitate with 0.5% ammonium oxalate while continuing to aspirate.
6. Transfer the oxalate precipitate to a 250-ml beaker with concentrated HNO_3. Place the filter stick in the beaker, and heat the sample on a hot plate until the precipitate separates from the filter stick. Rinse the filter stick inside and out with concentrated HNO_3, and remove the stick.
7. Evaporate the sample to near dryness. Add 50 ml concentrated HNO_3, and continue to evaporate. Repeat until the nitrate residue is colorless.
8. Transfer the residue to a 40-ml centrifuge tube, using a minimum quantity of concentrated HNO_3. Cool in a refrigerator overnight. Then centrifuge at 1500-1800 rpm for 10 minutes, and discard the supernatant solution.
9. Dissolve the precipitate in 5 ml $3\underline{N}$ HNO_3 and add 10 ml fuming nitric acid. Centrifuge, and discard the supernate.
10. Dissolve the precipitate in 5 ml distilled water. Add 3 drops of bromcresol green indicator. Add $6\underline{N}$ NH_4OH until the color changes from yellow to blue. Back-titrate with $0.5\underline{N}$ HNO_3 until the solution first turns yellow. Add 5 ml ammonium acetate buffer. Add 1.0 ml of barium carrier solution. Heat in a water bath, and add 1 ml of $1\underline{N}$ Na_2CrO_4. Warm until a definite barium chromate precipitate is noticed. Cool, and filter through Whatman No. 42 filter paper into a 250-ml beaker. Wash the precipitate with warm distilled water, and discard.
11. To the filtrate, add 5 drops of mixed rare earth carrier, 2 drops of concentrated HCl, and 5 drops 30% H_2O_2. Warm, and add concentrated NH_4OH dropwise until a rare earth precipitate forms. Filter through Whatman No. 42 filter paper, and wash the precipitate with $6\underline{N}$ NH_4OH. Discard the precipitate.

12. Evaporate the filtrate to approximately 10 ml. Transfer it to a 40-ml centrifuge tube using a minimum volume of concentrated NH_4OH. Add 5 ml concentrated NH_4OH and 2 ml of 3N Na_2CO_3. Mix thoroughly, cool, and centrifuge. Check for completeness of precipitation. When strontium carbonate precipitation is complete, centrifuge, and discard the supernatant liquid.
13. Dissolve the precipitate in no more than 6 ml of 3N HNO_3. Add 30 ml fuming nitric acid to precipitate strontium nitrate. Cool in a water bath, centrifuge, and discard the supernate. Repeat from the beginning of Step 13. RECORD DATE AND TIME OF CENTRIFUGATION AS THE BEGINNING OF YTTRIUM 90 INGROWTH. Store the precipitate for at least one week. [Note: Total radiostrontium may be determined at this point.]
14. Place 6.0 ml water into a 40-ml centrifuge tube for use as a volume standard for the following steps.
15. After a suitable ingrowth time (1 week minimum), dissolve the strontium nitrate precipitate in the centrifuge tube in no more than 6 ml of 3N HNO_3.
16. Add 30 ml fuming nitric acid to the centrifuge tube, and cool in a water bath to precipitate strontium nitrate.
17. Centrifuge. Decant the supernate containing the yttrium into a 250-ml beaker. RECORD DATE AND TIME OF DECANTATION AS THE END OF YTTRIUM 90 INGROWTH AND THE BEGINNING OF YTTRIUM 90 DECAY.
18. Dissolve the strontium nitrate precipitate with 6 ml distilled water, and repeat Steps 16 and 17, combining the supernates. Save the precipitate for Step 20.
19. Evaporate the combined supernates to a small volume, and transfer to a stainless steel planchet, using 3N HNO_3. Evaporate to dryness. Be extremely careful in transferring and evaporating the yttrium solution so as to obtain as close to 100% of the yttrium as possible, since a theoretical 100% recovery is used in calculating the strontium 90 activity. Count the activity of yttrium 90 in a low background beta counter.
20. Using distilled water, transfer the precipitate from Step 18 to a tared planchet. Evaporate to dryness, and determine the weight of strontium nitrate residue (in mg) to obtain the self-absorption

correction for counting data. If difficulty is encountered in drying the residue, flame the planchet over a burner, or place it in a muffle furnace at 400° C for 30 minutes. When completely dry, determine the total radiostrontium activity by counting in a low-background beta counter.

21. After counting, transfer the strontium nitrate residue from the planchet to a 250-ml volumetric flask using 3N HNO_3. Determine strontium recovery by flame spectrophotometry (see 3.3.1).

Calculations

$$\text{strontium 90 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F}$$

where A = net beta count rate of yttrium 90 (cpm)
B = recovery of strontium carrier
C = counter efficiency for yttrium 90 as yttrium nitrate (cpm/pCi)
D = sample volume (liters)
E = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time of decantation of the yttrium 90 supernate [Step 17] to the time of counting
F = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from the start of the ingrowth period [Step 13] until the time of decantation of the yttrium 90 supernate [Step 17]

$$\text{strontium 89 activity (pCi/liter)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G \times H + I \times J)\right]$$

where A = net beta count rate of radiostrontium (cpm)
B = counter efficiency for strontium 89 as strontium nitrate (cpm/pCi)
C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t

is the time from sample collection to the time of counting

D = recovery of strontium carrier

E = sample volume (liters)

F = strontium 90 activity (pCi/liter)

G = self-absorption factor for strontium 90 as strontium nitrate, obtained by comparing the density thickness of the sample (mg/cm^2) with a self-absorption calibration curve [Note: The self-absorption calibration curve should be prepared by making up a series of standard samples containing equal concentrations of ^{90}Sr activity per unit weight of strontium nitrate, but containing total weights of strontium nitrate ranging from zero to the maximum weight of strontium nitrate expected in the actual samples. The count rate per unit weight of solids in each standard sample is then divided by the count rate of the weightless samples, and this fraction is plotted as a function of density thickness (mg $Sr(NO_3)_2$ per cm^2 of planchet surface).]

H = counter efficiency for strontium 90 as strontium nitrate (cpm/pCi)

I = counter efficiency for yttrium 90 as yttrium nitrate (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from decantation of the yttrium nitrate solution [Step 17] to the time of counting

Evaluation of Data

Agreement of strontium concentrations determined by this method with those determined by other methods is well within ±5%.

References

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Murthy, G. K., J. E. Gaetjen, J. L. Kulp, and W. R. Eckelman. "A method for the elimination of ashing in strontium-90 determination of milk". *J Dairy Sci 43*:151-154 (1960)

3.2.3 Strontium 89, Strontium 90, and Barium 140

ION-EXCHANGE PROCEDURE — TBP Extraction

This procedure is applicable to the analysis of total radiostrontium, strontium 89, strontium 90, and barium 140 in whole or skim milk, or in evaporated milk diluted to the consistency of skim milk. This application includes milk containing fresh fission products as well as milk containing only long-lived fission products.

Milk analyzed by this procedure must be reasonably homogeneous since large amounts of separated cream or solids will impede or prevent the flow of milk through resin columns.* The milk must contain a preservative and should have been stored under refrigeration (32° to 34° F) for at least two weeks to allow the yttrium 90 daughter of strontium 90 to grow into equilibrium with its parent.

The method is easily followed by technicians. The Center's laboratories have established that three technicians working together can analyze 250 milk samples per month for total radiostrontium, strontium 90, and barium 140. In the past three years, these laboratories have used this method to analyze approximately 18,000 samples. Two laboratories of the National Center for Radiological Health currently use this method in their routine surveillance programs.

The ion-exchange apparatus consists of a cation-exchange resin column and an anion-exchange resin column. Strontium, barium, and calcium are adsorbed on the cation resin and yttrium is adsorbed on the anion resin. This separation allows the nuclides to be analyzed individually. By passing milk over both columns and analyzing the eluates, the concentrations of total radiostrontium, strontium 89, strontium 90, and barium 140 may be determined. If only the strontium 90 concentration is required, the eluate from the cation column may be discarded. If only total radiostrontium and barium 140 concentrations are required, the anion column is not used, and the eluate from the cation column alone is analyzed.

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* Procedures for ashed milk (see 3.1.2, p. 3-4) or 3.2.3 BATCH ION EXCHANGE PROCEDURE, p. 3-33 can be used for non-homogeneous milk.

However, if the concentration of strontium 89 is required, both column eluates must be analyzed, since strontium 89 concentration is computed as the difference between total radiostrontium and strontium 90 concentrations.

Principle of Method

A citrate complex of yttrium, strontium, and barium carriers at the pH of milk is added to the milk sample. The mixture is then passed successively through cation- and anion-exchange resin columns. Strontium, barium, and calcium are adsorbed on the cation-exchange resin, and the yttrium carrier with the yttrium 90 daughter of strontium 90 is retained on the anion-exchange resin.

The yttrium is eluted from the anion resin with hydrochloric acid and precipitated as the oxalate. Lanthanum 140, which may be a contaminant, is removed by dissolving yttrium oxalate in concentrated nitric acid and extracting yttrium from the solution into an equal volume of pre-equilibrated tributyl phosphate. The lanthanum 140 remains in the concentrated nitric acid to be discarded. Yttrium is re-extracted from the organic phase with dilute nitric acid and precipitated as the oxalate. The precipitate is weighed to determine recovery of yttrium carrier, then counted for yttrium 90 activity.

Strontium, barium, and calcium are eluted from the cation-exchange resin with sodium chloride solution. Following dilution of the eluate, the alkaline earths are precipitated as carbonates. The carbonates are then converted to nitrates, and strontium and barium nitrate are precipitated. The nitrate precipitate is dissolved, and barium is precipitated as the chromate, purified as the chloride, and then counted to determine barium 140. From the supernate, strontium is precipitated as the nitrate, dissolved in water, and reprecipitated as strontium nitrate. The nitrate is converted to the oxalate, which is filtered, weighed to determine strontium carrier recovery, and counted for "total radiostrontium".

The concentration of strontium 89 is calculated as the difference between the activity for "total radiostrontium" and the activity due to strontium 90.

Reagents

ammonium acetate buffer: pH 5.0
ammonium hydroxide, NH_4OH: concentrated (15N)
ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 1N
anion-exchange resin: Dowex 1-X8 (Cl^- form, 50-100 mesh)
carrier solutions:
  Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
  Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20 mg Sr^{+2} per ml
  Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml
cation-exchange resin: Dowex 50W-X8 (Na^+ form, 50-100 mesh)
citrate solution: 3N (pH 6.5)
diethyl ether, $(C_2H_5)_2O$: anhydrous
ethyl alcohol, C_2H_5OH: absolute (100%), 95%
hydrochloric acid, HCl: concentrated (12N), 6N*, 2N*
hydrochloric acid–diethyl ether, $HCl–(C_2H_5)_2O$: 5:1 v/v
nitric acid, HNO_3: fuming (90%), concentrated (16N)*, 14N*, 6N, 0.1N*
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N*
sodium carbonate, Na_2CO_3: 3N
sodium chloride, NaCl: 4N
sodium chromate, Na_2CrO_4: 3N
tri-*n*-butyl phosphate [TBP], $(C_4H_9)_3PO_4$: pre-equilibrated with 14N HNO_3*

* Starred reagents are used only in processing the anion column effluent to determine strontium 90 concentrations. (Part A.)

Apparatus

ion-exchange system: The apparatus for this system is illustrated in Figure 3.2-1. It consists of three glass components connected one above the other for gravity flow. At the top is a graduated, 1-liter glass separatory funnel which serves as the reservoir. Below it is connected a 250-ml glass column, 5 cm in diameter and 25 cm long, which serves as the cation column. Below this is connected the anion column, a 30-ml glass column, 1.9 cm in diameter and 10.5 cm long. Both columns have extra coarse, fritted glass disks at the bottom.

Five milliliters of distilled water are placed in the 30-ml

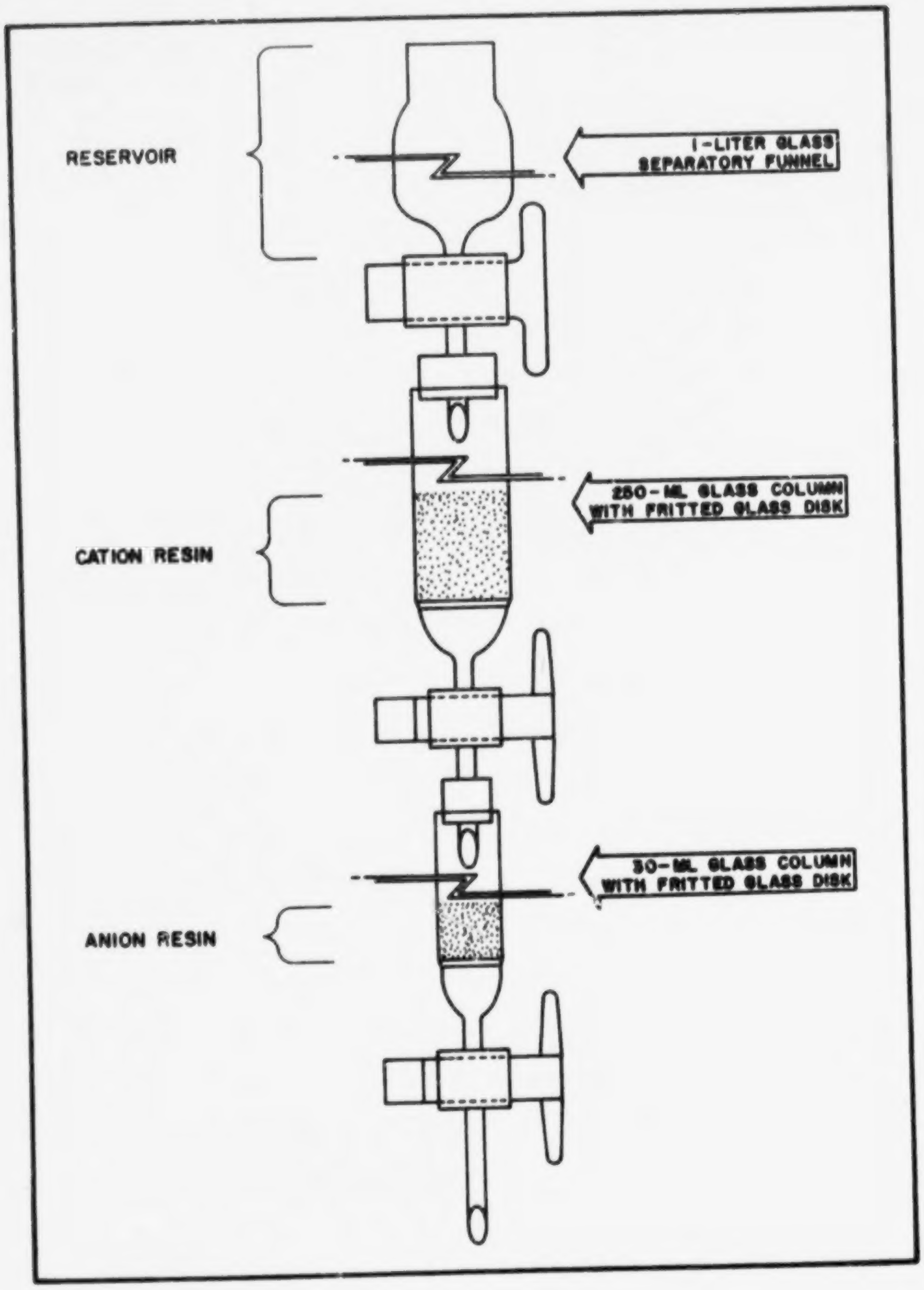
RESERVOIR
1-LITER GLASS SEPARATORY FUNNEL
250-ML GLASS COLUMN WITH FRITTED GLASS DISK
CATION RESIN
30-ML GLASS COLUMN WITH FRITTED GLASS DISK
ANION RESIN

Figure 3.2-1 Ion-exchange system

column, and 15 ml Dowex 1 resin are poured into it. The cation column is filled by adding 170 ml Dowex 50W resin in the same way.

Millipore filtering apparatus (Pyrex Hydrosol Microanalysis Filter Holder)

Millipore Type OH membrane filter, 1.5-μ pore size, 2.5-cm diameter

low-background beta counter

Procedure

Part A. Analysis of strontium 90

1. Place 1 liter of milk into the graduated reservoir. Pipette 1.0 ml each of yttrium, strontium, and barium carrier solutions into 10 ml of citrate solution; swirl to mix and dissolve the barium citrate which forms. Transfer this mixture quantitatively to the milk with 5 ml distilled water, and mix well.
2. Open stopcocks of reservoir, anion column, and cation column, in that order. NOTE THE TIME. Control flow rate at 10 milliliters per minute (ml/min) with the anion column stopcock. Check occasionally by collecting effluent for 1 minute in a graduated cylinder. Stop flow when just enough milk remains in columns to cover resin. NOTE THE TIME. Discard effluent milk. RECORD MIDPOINT OF THE ELUTION PERIOD AS THE BEGINNING OF YTTRIUM 90 DECAY.
3. Replace the milk reservoir with a separatory funnel containing 300 ml of warm distilled water, and let the water flow through the columns at approximately 10 ml/min to displace the milk. Stop the flow when just enough water remains in the columns to cover the resin. Discard the effluent water.
4. Separate the columns. In order to collect eluate for "total radiostrontium", barium, and calcium determinations, and to regenerate the cation column for subsequent use, follow Step 5 of Part B, p. 3-26. For strontium 90 determination, proceed with Step 5 of Part A below.
5. Attach a separatory funnel containing 100 ml of 2N HCl to the top of the anion column. Let the acid flow at 2 ml/min. Discard effluent until its pH drops to 2, as indicated by universal pH paper (after 10 to 20 ml).

   [Note: Before milk is passed over the column, 10 ml of tincture of merthiolate (1:1000) containing eosin dye can be thoroughly mixed with the anion resin to act as an indicator when eluting with 2N HCl. The color change indicates the approximate point at which the pH drops to 2. However, universal pH paper is still used to obtain a more accurate point at which the pH change occurs.] Collect the next 10 ml of eluate, stop the flow of acid, and remove the separatory funnel. Stir the anion resin thoroughly with a glass stirring rod. Wash the stirring rod with a small amount of 2N HCl and add this acid to the resin column. Re-attach the separatory funnel, and continue eluting with 2N HCl. Collect the next 25 ml of eluate to a total volume of 35 ml. Process this eluate for strontium 90 analysis beginning at Step 7, below.

6. Allow remaining 2N HCl to flow at 10 ml/min to wash and recharge the column. Discard the effluent. Wash the resin with 100 ml of distilled water and discard the effluent water. If necessary, backwash or slurry the resin to remove trapped milk particles.
7. To precipitate yttrium oxalate from the 35 ml of anion eluate, add 5 ml of 2N oxalic acid, and using a pH meter adjust the pH to 1.5 with approximately 2.5 ml of concentrated NH_4OH. Stir, heat in a hot water bath to near boiling, and cool in an ice bath approximately 20 minutes. Centrifuge, and discard the supernatant liquid.
8. If fresh fission products are not present in the sample, as determined from gamma spectral analysis of the whole milk, the lanthanum extraction (Steps 9 through 14) may be omitted. If lanthanum extraction is not required, follow Step 8a; then proceed to Step 15. If the gamma spectrum has not been analyzed, or if fresh fission products are present, follow Steps 9 through 19.
   - 8a. Wash the yttrium oxalate precipitate with 10 ml of hot distilled water. Centrifuge; decant and discard the supernate. Dissolve the precipitate in 1 ml of 6N HCl and 15 ml of hot distilled water. If insoluble material remains, centrifuge, and transfer the supernate to another 40-ml centrifuge tube. Continue working with the supernate at Step 15.
9. Add 10 ml of concentrated HNO_3 to dissolve the precipitate obtained in Step 7. Transfer the contents of the centrifuge tube to a 60-ml separatory funnel. Wash the tube with 10 ml of pre-equilibrated TBP, and

add this TBP to the separatory funnel.

10. Equilibrate by shaking for approximately 2-3 minutes; allow phases to separate. Drain the acid phase away and discard.
11. Add 15 ml of 14N HNO_3 to the separatory funnel, and equilibrate again for approximately 2-3 minutes; allow phases to separate. Drain the acid phase away and discard.
12. Repeat Step 11.
13. Remove yttrium from the organic phase by adding 15 ml of distilled water and equilibrating for approximately 2-3 minutes. Allow phases to separate, and drain the aqueous phase into a 40-ml centrifuge tube.
14. Repeat Step 13 using 15 ml of 0.1N HNO_3 instead of water, and drain the acid phase into the 40-ml centrifuge tube which contains the aqueous phase from Step 13.
15. To precipitate yttrium oxalate, add 5 ml of 2N oxalic acid to the aqueous solution, and using a pH meter adjust the pH to 1.5 with approximately 2 ml of concentrated NH_4OH. Stir while cooling in an ice bath approximately 20 minutes. Centrifuge, and discard the supernate.
16. Label and weigh a stainless steel planchet together with a 2.5 cm diameter membrane filter. Place the membrane filter into a Millipore filtering apparatus.
17. Take up the precipitate in 10 ml of cold distilled water and transfer it to the filtering apparatus. Wash with one 10-ml portion of cold distilled water, using the water to wash out the centrifuge tube. Dry the precipitate with three 20-ml portions of 95% ethyl alcohol and three 10-ml portions of diethyl ether. Continue suction for 2 minutes.
18. Carefully transfer the membrane filter with the oxalate precipitate to the pre-weighed stainless steel planchet. Let stand at room temperature for 10-15 minutes; then weigh. Calculate the recovery of yttrium carrier as yttrium oxalate $[Y_2(C_2O_4)_3 \cdot 9H_2O]$.
19. Count the beta activity of the yttrium oxalate precipitate in a low background beta counter. Be sure the membrane filter remains centered in the planchet to maintain constant geometry during counting. Count again after three days, or after three weeks when yttrium activity is essentially gone, to confirm that yttrium 90 is not contaminated by other radionuclides.

Part B. Analysis of total radiostrontium (^{89}Sr) and barium 140
[Note: If this analysis is performed in conjunction with the strontium 90 analysis (Part A), begin with Step 5 below.]

1. Place 1 liter of milk into the graduated reservoir. Pipette 1.0 ml each of the yttrium, strontium, and barium carriers into 10 ml of 3N citrate solution; swirl to mix and dissolve barium citrate. Quantitatively transfer this mixture to the milk with 5 ml of distilled water, and mix well.
2. Open stopcocks of the reservoir, anion column, and cation column, in that order. Control flow rate with anion column stopcock at 10 milliliters per minute (ml/min). Check occasionally by collecting effluent for 1 minute in a graduated cylinder. Stop flow when just enough milk remains in columns to cover resin. Discard the effluent milk.
3. Replace the milk reservoir with a separatory funnel containing 300 ml of warm distilled water, and wash the column with water to displace milk. Stop the flow when just enough water remains in columns to cover the resin. Discard effluent water.
4. Separate the columns. If strontium 90 analysis is required, process the anion column according to the procedures given in Part A, beginning with Step 5, p. 3-23.
5. To the top of the cation column, attach a 1-liter separatory funnel containing 1 liter of 4N NaCl. Allow the NaCl solution to flow at 10 ml/min to elute alkali metal and alkaline earth ions and also to recharge the column. Leave enough eluant to cover the resin to a depth of 2 cm. Collect eluate in a graduated 2-liter beaker until the total valume is 1 liter. An aliquot of this NaCl eluate can be taken for the determination of stable calcium (see 3.3.2 Calcium). To remove excess NaCl from the resin, place 500 ml of distilled water in the separatory funnel and let it flow into another beaker at 10 ml/min. Discard this washing. If the resin clogs with extended use, backwash or slurry the resin with water to remove trapped milk particles.
6. Dilute the remaining NaCl eluate to 1500 ml with distilled water.
7. Heat this solution to 85-90° C on a hot plate and add, with stirring, 100 ml of 3N Na_2CO_3. Stir gently while on the hot plate to prevent

bumping. Remove from the hot plate, cool, and decant most of the supernate. Transfer the carbonate precipitate to a 250-ml centrifuge bottle. Centrifuge, and decant the supernate.

8. Wash the precipitate twice with 50-ml portions of distilled water. Dry in an oven at 110° C for 4 hours.
9. Remove from the oven and cool the precipitate to room temperature. Add approximately 10 ml of 6N HNO_3 to the precipitate, and stir vigorously, using a magnetic stirrer, until the precipitate is dissolved. Filter the solution through Whatman No. 4 filter paper into a 40-ml graduated centrifuge tube. Discard the filter paper and its contents.
10. To the filtrate, add a sufficient volume of fuming nitric acid to obtain approximately 70% nitric acid concentration (see Table 3.2-1). Stir and cool in an ice bath. Centrifuge, and decant the supernate.

Table 3.2-1 Nitric acid proportions for strontium and barium precipitations

Volume of 6N HNO_3 (ml)	Volume of Fuming HNO_3 to be Added (ml)	HNO_3 Concentration Obtained (%)
8	15	69.8
9	17	69.9
10	19	70.0
11	21	70.1
12	22	69.5
13	24	69.6
14	26	69.7
15	28	69.8
16	30	69.8

11. Dissolve the precipitate in 5 ml of distilled water. Add 5 ml of ammonium acetate buffer, and check for a pH of 5 with pH paper. Add additional buffer solution if necessary.
12. To precipitate barium chromate, heat the solution in a water bath, and add, dropwise and with stirring, 1 ml of 3N Na_2CrO_4. Centrifuge,

and decant the supernate into a 40-ml centrifuge tube. If barium 140 analysis is desired, work with the precipitate, and follow Steps 13 through 18; otherwise, continue working with the supernate beginning at Step 19.

13. Add approximately 5 ml of concentrated HCl to the barium chromate precipitate. Heat in a water bath until this yellow precipitate is dissolved and a white, granular barium chloride precipitate remains. Chromic ion [Cr^{+3}] gives the solution its green color.
14. Cool in an ice bath and add 20 ml of cold HCl—diethyl ether reagent. Stir, centrifuge, and decant the supernate. The remaining barium chloride precipitate [$BaCl_2 \cdot 2H_2O$] should be pure white. If it is not, repeat the HCl—diethyl ether application. RECORD THE TIME OF DECANTATION AS THE BEGINNING OF LANTHANUM 140 INGROWTH.
15. Label and weigh a stainless steel planchet together with 2.4-cm diameter Whatman No. 542 filter paper. Place the filter paper into the Millipore filtering apparatus.
16. Transfer the precipitate onto the filter paper with several 10-ml portions of cold absolute ethyl alcohol. Use a total volume of at least 30 to 40 ml of absolute ethyl alcohol.
17. Transfer filter paper with precipitate to the pre-weighed stainless steel planchet; dry in an oven at 100° C for one hour. Cool in a desiccator 10-15 minutes. Weigh the sample, and calculate the recovery of barium carrier as anhydrous barium chloride [$BaCl_2$]. [Note: Oven drying can be omitted by leaving the alcohol-treated precipitate in contact with the atmosphere until constant weight is achieved (approximately 3 hours). The recovery of barium carrier is then calculated from the weight of barium chloride [$BaCl_2 \cdot 2H_2O$].]
18. Count the precipitate on the planchet for barium 140 activity in a low-background beta counter. Be sure the filter is centered in the planchet to maintain constant geometry during counting.
19. To the supernate from Step 12, add 30 ml of fuming nitric acid; stir, and cool in an ice bath to precipitate strontium nitrate. Centrifuge, and decant the supernate.
20. Dissolve the strontium nitrate precipitate in 10 ml of distilled water. Add 30 ml of fuming nitric acid, stir, cool in an ice bath, centrifuge the sample, and decant the supernate. RECORD THE TIME OF DECANTATION

AS THE BEGINNING OF YTTRIUM 90 INGROWTH.

21. Dissolve the strontium nitrate precipitate in 10 ml of distilled water and add 3 ml of concentrated NH_4OH. Heat to near boiling in a hot water bath, and add 5 ml of $1\underline{N}$ ammonium oxalate to precipitate strontium oxalate. Cool in an ice bath. Centrifuge, and decant the supernate.

22. Label and weigh a stainless steel planchet together with a 2.5-cm diameter Millipore Type OH filter. Place the filter into the Millipore filtering apparatus.

23. Transfer the strontium oxalate precipitate to the filtering apparatus with three 10-ml portions of diethyl ether. Continue suction for two minutes.

24. Carefully transfer the filter with precipitate to the pre-weighed stainless steel planchet. Let stand at room temperature for 10-15 minutes; then weigh. Calculate the recovery of strontium carrier. [Note: Recovery of strontium carrier can also be determined by dissolving the precipitate after if has been counted and measuring its strontium concentration by flame spectrophotometry (see 3.3.1 Strontium Carrier, p. 3-43).]

25. Count the precipitate in a low-background beta counter for "total radiostrontium" activity. Be sure the filter is centered in the planchet to maintain constant geometry during counting.

Calculations

Part A.

$$\text{strontium 90 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of yttrium carrier

C = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

D = sample volume (liters)

E = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from midpoint of the elution time of the milk [Step 2] to the time of counting

F = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from collection of the milk sample to the time of passage through the column [Step 2]

Part B.

$$\text{strontium 89 activity (pCi/liter)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G \times H + I \times J)\right]$$

where A = net beta count rate of "total radiostrontium" (cpm)

B = counter efficiency for counting strontium 89 as strontium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting

D = recovery of strontium carrier

E = volume of milk sample (liters)

F = strontium 90 concentration (pCi/liter) from Part A

G = self-absorption factor for strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter, obtained from a self-absorption curve prepared by plotting the fraction of a standard activity absorbed against density thickness of the sample (mg/cm^2) [See SECTION 1. INSTRUMENTATION, and 3.2.2, p. 3-12]

H = counter efficiency for counting strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

I = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from the last decantation of the nitric acid supernate from the strontium nitrate precipitate (Step 20) to the time of counting

$$\text{barium 140 activity (pCi/liter)} = \frac{A}{[B \times C \times D]\ [E + (1.15 \times F \times G)]}\ .$$

where A = net beta count rate (cpm)

B = recovery of barium carrier

C = volume of milk sample (liters)

D = correction factor $e^{-\lambda t}$ for decay of barium 140, where t is the time from collection of the sample to the time of counting

E = counter efficiency for counting barium 140 on a 2.4-cm diameter filter paper (cpm/pCi)

F = counter efficiency for counting lanthanum 140 on a 2.4-cm diameter filter paper (cpm/pCi)

G = correction factor $1-e^{-0.015t}$ for the ratio of lanthanum 140 activity to barium 140 activity, where t is the time in hours from the barium separation [Step 14] to the time of counting

1.15 = the ratio of lanthanum 140 activity to barium 140 activity when the mixture is in transient equilibrium. It is obtained by reducing the terms in the "ingrowth equation" for transient equilibrium when barium 140 is corrected for decay from the time of sample collection to the time of lanthanum 140 separation.

Evaluation of Data

The standard deviation of replicate analyses for strontium 90 by this ion-exchange procedure has consistently been ±1.5 pCi/liter or ±5%, whichever is greater.

The standard deviations of replicate analyses for strontium 89 and for barium 140 have consistently been ±5 pCi/liter or ±5%, whichever is greater.

References

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BATCH ION-EXCHANGE PROCEDURE – TBP Extraction

This procedure is applicable to any liquid milk, including that which is no longer homogeneous, *i.e.*, soured, curdled, or containing excessive cream. Analyses for total radiostrontium (strontium 89), strontium 90, and barium 140 may be made. Nonhomogeneous milk can also be ashed and analyzed as described in 3.1.2, page 3-4 of this section.

This method is very similar to the ION-EXCHANGE PROCEDURE described on page 3-19. The primary difference is in the strontium 90 analysis. The ION-EXCHANGE PROCEDURE allows for the ingrowth of yttrium 90 in the milk itself. The BATCH ION-EXCHANGE PROCEDURE involves separating the strontium from other ~~nuclides in the milk~~ and subsequent ingrowth of yttrium 90. As a result, this procedure is more time-consuming.

Principle of Method

Milk, with added strontium and barium carriers, is thoroughly mixed with cation-exchange resin. The resin is washed and placed in a column. The alkaline earths are eluted with sodium chloride solution and precipitated as carbonates, which are then converted to nitrates. The nitrate precipitate is dissolved. From this solution, barium is precipitated as the chromate and purified as the chloride, which is counted to determine barium 140.

Strontium is precipitated from the supernatant solution as the nitrate, purified by reprecipitation, and stored for yttrium 90 ingrowth. After one to two weeks, the strontium nitrate is dissolved, yttrium carrier is added, and strontium is reprecipitated from concentrated nitric acid. Yttrium is then extracted from the solution with tributyl phosphate, re-extracted with dilute nitric acid, and precipitated as the oxalate. The yttrium oxalate is weighed to determine recovery of yttrium carrier, and then counted to determine yttrium 90 activity. The strontium nitrate is dissolved and strontium is precipitated as strontium oxalate. The oxalate precipitate is filtered, weighed to determine strontium carrier recovery, and counted for "total radiostrontium" activity.

Strontium 89 activity is calculated from the difference between "total radiostrontium" activity and the previously determined activity of strontium 90.

Reagents

ammonium acetate buffer: pH 5.0

ammonium hydroxide, NH_4OH: concentrated (15N)

ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 1N

carrier solutions:

- Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
- Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20 mg Sr^{+2} per ml
- Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml

cation-exchange resin: Dowex 50W-X8 (Na^+ form, 50-100 mesh)

diethyl ether, $(C_2H_5)_2O$: anhydrous

ethyl alcohol, C_2H_5OH: absolute (100%), 95%

hydrochloric acid, HCl: concentrated (12N)

hydrochloric acid–diethyl ether, $HCl-(C_2H_5)_2O$: 5:1 v/v

nitric acid, HNO_3: fuming (90%), concentrated (16N), 14N, 8N, 6N, 0.1N

oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N

sodium carbonate, Na_2CO_3: 3N

sodium chloride, NaCl: 4N

sodium chromate, Na_2CrO_4: 3N

tri-*n*-butyl phosphate [TBP], $(C_4H_9)_3PO_4$: pre-equilibrated with 14N HNO_3

Apparatus

ion-exchange column, 250-ml (5-cm diameter, 25-cm length), with extra coarse fritted glass disk in bottom

low-background beta counter

Millipore filtering apparatus (Pyrex Hydrosol Microanalysis Filter Holder)

Millipore Type OH membrane filter, 1.5-μ pore size, 2.5-cm diameter

Procedure

1. Place 1 liter of nonhomogeneous milk in a 2-liter beaker, and add 140 ml of cation-exchange resin. Then pipette into the milk–resin mixture, 1.0 ml each of strontium and barium carrier solutions.
2. Stir for one hour with a magnetic stirrer. Then let the resin settle and decant the supernate. Wash milk from the resin with warm distilled water, and decant the water. If any of the resin is lost, a calcium determination cannot be made from the sodium chloride eluate.

3. Transfer the resin to the ion-exchange column. To the top of the column, attach a 500-ml separatory funnel containing 500 ml of 4N NaCl.
4. Allow the NaCl eluant to flow at 10 milliliters per minute (ml/min). Collect the eluate in a graduated 2-liter beaker. When only enough eluant remains to cover the resin to a depth of 2 cm, place 500 ml of distilled water in the separatory funnel and allow it to flow at 10 ml/min until the combined NaCl—water eluate reaches a volume of 1 liter. [This procedure simultaneously washes and recharges the resin for further use.]

   [Note: If a calcium determination is desired, remove a 20-ml aliquot of the NaCl—water eluate and analyze it for calcium by the PERMANGANATE TITRATION procedure described in 3.3.2, page 3-49.]
5. Dilute the combined eluate to 1500 ml with distilled water. Heat the solution to 85-90° C on a hot plate and add, with stirring, 100 ml of 3N Na_2CO_3. Gently stir the solution as it heats to prevent bumping. When the carbonate precipitate is fully developed, remove the beaker from the hot plate. Cool, and decant most of the supernate. Transfer the precipitate to a 250-ml centrifuge bottle with distilled water. Centrifuge, and decant the supernate.
6. Wash the precipitate twice with 50-ml portions of distilled water. Dry in an oven at 110° C for at least 4 hours.
7. When completely dry, remove the precipitate from the oven and let it cool to room temperature. Then add to the precipitate approximately 10 ml of 6N HNO_3, and stir vigorously with a magnetic stirrer until the carbonate is dissolved. Filter the solution through Whatman No. 4 filter paper into a 40-ml graduated centrifuge tube. Discard the filter paper and its contents.
8. To the filtrate, add a sufficient volume of fuming nitric acid to obtain a 70% nitric acid concentration (see Table 3.2-1, p. 3-28). Stir the mixture, and cool in an ice bath to develop the strontium—barium nitrate precipitate. Centrifuge, and decant the nitric acid supernate.
9. Dissolve the precipitate in 5 ml of distilled water. Add 5 ml of ammonium acetate buffer and check for a pH of 5 with pH paper. Add additional buffer solution if necessary.
10. To precipitate barium chromate, heat the buffered solution in a water

bath and add, dropwise with stirring, 1 ml of 3N Na_2CrO_4. Centrifuge, and decant the supernate into a 40-ml centrifuge tube.

[Note: If barium 140 analysis is desired, work with the precipitate and follow Steps 11 through 16; otherwise, work with the supernate beginning at Step 17.]

11. Add approximately 5 ml of concentrated HCl to the barium chromate precipitate. Heat in a water bath until this yellow precipitate is dissolved and a white, granular barium chloride precipitate remains. Chromic ion [Cr^{+3}] gives the solution its green color.
12. Cool the mixture in an ice bath, add 20 ml of cold HCl—diethyl ether reagent, and stir. Centrifuge, and decant the supernate. The remaining barium chloride precipitate [$BaCl_2 \cdot 2H_2O$] should be pure white. If it is not, repeat the cold HCl—diethyl ether application. RECORD THE TIME OF FINAL DECANTATION AS THE BEGINNING OF LANTHANUM 140 INGROWTH.
13. Label and weigh a stainless steel planchet together with a 2.4-cm diameter Whatman No. 542 filter paper. Place the filter paper into the Millipore filtering apparatus.
14. Transfer the barium chloride precipitate onto the filter paper with several 10-ml portions of cold absolute ethyl alcohol. Use at least 30-40 ml of absolute ethyl alcohol.
15. Transfer the filter paper containing the precipitate to the pre-weighed stainless steel planchet, and dry in an oven at 100° C for one hour. Cool in a desiccator 10-15 minutes. Then weigh the precipitate, and calculate the recovery of barium carrier as anhydrous barium chloride [$BaCl_2$].

    [Note: Oven drying can be omitted by leaving the alcohol-treated precipitate in contact with the atmosphere until constant weight is achieved (approximately 3 hours). The recovery of barium carrier is then calculated from the weight of barium chloride [$BaCl_2 \cdot 2H_2O$].]
16. Count the precipitate on the planchet in a low-background beta counter for barium 140 activity. Be sure the filter is centered in the planchet to maintain constant geometry during counting.
17. To the supernate from Step 10, add 30 ml of fuming nitric acid. Stir, and cool in an ice bath. Centrifuge, and discard the nitric acid supernate.
18. Dissolve the strontium nitrate precipitate in 10 ml of distilled water.

Add 30 ml of fuming nitric acid, stir, and cool in an ice bath. Centrifuge, and decant the supernate. RECORD THE TIME OF DECANTATION AS THE BEGINNING OF YTTRIUM 90 INGROWTH. Drain excess HNO_3 from the centrifuge tube by inverting the tube on paper towels.

19. Store the strontium nitrate precipitate for ingrowth of yttrium 90 from one to two weeks.
20. At the end of the ingrowth period, pipette 1.0 ml of yttrium carrier solution into the centrifuge tube, and add 1.0 ml of 8N HNO_3. Warm gently to dissolve the strontium nitrate precipitate. Add 10 ml of fuming nitric acid, and cool in an ice bath for 10 minutes. Centrifuge, and decant the supernate as quantitatively as possible into a 60-ml separatory funnel. RECORD THE TIME OF DECANTATION AS THE BEGINNING OF YTTRIUM 90 DECAY IN THE SUPERNATE, AND OF YTTRIUM 90 INGROWTH INTO THE TOTAL STRONTIUM PRECIPITATE. Save the precipitate. Drain excess HNO_3 from the centrifuge tube by inverting the tube on paper towels.
21. To the acid solution in the separatory funnel, add 4 ml of distilled water to make the solution 14N in nitric acid. Add 10 ml of preequilibrated TBP to this solution.
22. Equilibrate by shaking for approximately 2-3 minutes; allow the phases to separate. Drain off the acid phase and discard it.
23. Add 15 ml of 14N HNO_3 to the separatory funnel, and shake again for approximately 2-3 minutes; allow the phases to separate. Drain off and discard the acid phase.
24. Repeat Step 23.
25. Remove yttrium from the organic phase by adding 15 ml of distilled water and shaking for approximately 2-3 minutes. Allow the phases to separate and drain the aqueous phase into a 40-ml centrifuge tube.
26. Repeat Step 25 using 15 ml of 0.1N HNO_3 instead of water, and drain the acid phase into the same 40-ml centrifuge tube used in Step 25.
27. To precipitate yttrium oxalate, add to the aqueous extract 5 ml of 2N oxalic acid, and adjust the pH to 1.5 with approximately 2 ml of concentrated NH_4OH (using a pH meter). Stir while cooling in an ice bath approximately 20 minutes. Centrifuge, and discard the supernate.
28. Label and weigh a stainless steel planchet together with a 2.5-cm diameter membrane filter. Place the membrane filter into a Millipore filtering apparatus.

29. Take up the precipitate in 10 ml of cold distilled water and transfer it to the filtering apparatus. Wash with one 10-ml portion of cold water, first using the water to wash out the centrifuge tube. Dry the precipitate in the filter with three 20-ml portions of 95% ethyl alcohol and three 10-ml portions of diethyl ether. Continue suction for two minutes.
30. Carefully transfer the membrane filter with the dry precipitate to the pre-weighed stainless steel planchet. Let stand at room temperature. for 10-15 minutes; then weigh. From the weight of the precipitate, calculate the recovery of yttrium carrier as yttrium oxalate [$Y_2(C_2O_4)_3 \cdot 9H_2O$].
31. Determine the yttrium 90 activity by counting the yttrium oxalate precipitate in a low-background beta counter. Be sure the filter is centered in the planchet to maintain constant geometry during counting. Count again after three days, or after three weeks when yttrium activity is essentially gone, to confirm that yttrium 90 is not contaminated by other radionuclides.
32. Dissolve the strontium nitrate precipitate (obtained in Step 20) in 10 ml of distilled water, and add 3 ml of concentrated NH_4OH. Heat to near boiling in a hot water bath, and add 5 ml of 1$\underline{N}$ ammonium oxalate to precipitate strontium oxalate. Cool in an ice bath, centrifuge, and decant the supernate.
33. Label and weigh a stainless steel planchet together with a 2.5-cm diameter Millipore Type OH filter. Place the filter into the Millipore filtering apparatus.
34. Transfer the strontium oxalate precipitate to the filtering apparatus using three 10-ml portions of cold distilled water. Wash the precipitate with three 10-ml portions of 95% ethyl alcohol, and dry with three 10-ml portions of diethyl ether. Continue suction for two minutes.
35. Transfer the filter with precipitate to the pre-weighed stainless steel planchet. Let stand at room temperature for 10-15 minutes; then weigh. Calculate the recovery of strontium carrier as strontium oxalate [$SrC_2O_4 \cdot H_2O$].

    [Note: Strontium carrier recovery can also be determined by flame spectrophotometry. After the precipitate has been counted, analyze it for strontium by the procedure described in 3.3.1 Strontium Carrier, page 3-43.]

36. Count "total radiostrontium" activity of the precipitate in a low background beta counter.

Calculations

$$\text{strontium 90 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F \times G}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of strontium carrier

C = recovery of yttrium carrier

D = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

E = sample volume (liters)

F = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from the decantation of the yttrium 90 supernate [Step 20] to the time of counting

G = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from the start of the ingrowth period [Step 18] until the time of decantation of the yttrium 90 supernate [Step 20]

$$\text{strontium 89 activity (pCi/liter)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G{\times}H + I{\times}J)\right]$$

where A = net beta count rate of "total radiostrontium" (cpm)

B = counter efficiency for counting strontium 89 as strontium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting

D = recovery of strontium carrier

E = volume of milk sample (liters)

F = strontium 90 activity (pCi/liter)

G = self-absorption factor for strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter, obtained from a self-absorption curve prepared by plotting the fraction of a standard activity absorbed against density thickness (mg/cm^2) of the sample [See SECTION 1. INSTRUMENTATION, and 3.2.2, page 3-12]

H = counter efficiency for counting strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

I = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from the beginning of the ingrowth period [Step 18] until the time of decantation of the yttrium 90 supernate [Step 20]

$$\text{barium 140 activity (pCi/liter)} = \frac{A}{[B \times C \times D][E + (1.15 \times F \times G)]}$$

where A = net beta count rate (cpm)

B = recovery of barium carrier

C = volume of milk sample (liters)

D = correction factor $e^{-\lambda t}$ for decay of barium 140, where t is the time from collection of the sample to the time of counting

E = counter efficiency for counting barium 140 as barium chloride mounted on a 2.4-cm diameter filter paper (cpm/pCi)

F = counter efficiency for counting lanthanum 140 as a chloride precipitate mounted on a 2.4-cm diameter filter paper (cpm/pCi)

G = correction factor $1-e^{-0.015t}$ for the ratio of lanthanum 140 activity to barium 140 activity, where t is the time in hours from the barium separation [Step 12] to the time of counting

1.15 = the ratio of lanthanum 140 activity to barium 140 activity when the mixture is in transient equilibrium. This factor is obtained by reducing the "ingrowth equation" for transient equilibrium when barium 140 is corrected for decay from the time of lanthanum 140 separation.

Evaluation of Data

Standard deviations of replicate analyses are:

for strontium 90, ±1.5 pCi/liter or ±5%, whichever is greater,
for strontium 89, ±5 pCi/liter or ±5%, whichever is greater, and
for barium 140, ±5 pCi/liter or ±5%, whichever is greater.

References

Butler, F. E. "Sr^{90} monitoring at the Savannah River Plant". Report No. DP-473, E. I. Du Pont de Nemours & Co., Aiken (1960)

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

3.2.4 Gamma Emitters

In the National Center's laboratories, milk samples are routinely analyzed by gamma spectrometry for iodine 131, cesium 137, and barium 140. The potassium content of milk is determined by spectral analysis of potassium 40. No special preparation of the milk samples is required other than to pour a measured (3.5-liter) aliquot into the inverted-well type sample container which fits over the right-cylindrical sodium iodide crystal detector which these laboratories use.

SECTION 1. INSTRUMENTATION discusses the determination of gamma emitters in milk by gamma pulse height analysis in parts 1.1.3 Gamma Spectrometry and 1.1.4 Calculation of Results and Counting Error.

References

Kahn, B., G. K. Murthy, C. Porter, G. R. Hagee, G. J. Karches, and A. S. Goldin. *Rapid Methods for Estimating Fission Product Concentrations in Milk.* Public Health Service Publication No. 999-R-2, Environmental Health Series, Radiological Health (1963)

Ibid., p. 17

3.3 DETERMINATION OF STABLE ELEMENTS

3.3.1 Strontium Carrier

FLAME PHOTOMETRIC METHOD

The recovery of strontium carrier may be determined flame photometrically as well as by gravimetric methods. The latter are discussed in the appropriate steps of procedures for analysis of radiostrontium (see 3.2 DETERMINATION OF RADIOACTIVITY).

Although the following method was specifically designed for use with the ion-exchange procedures given in 3.2.3, it may also be used in conjunction with the TCA PRECIPITATION METHOD (3.2.2) by varying the dilutions of samples and standards.

Principle of Method

Strontium oxalate, precipitated in procedures for analysis of total radiostrontium, is dissolved in acid and diluted with water. Strontium in the solution is determined flame photometrically at a wave length of 460 mu, using an oxy-acetylene flame.

Reagents

nitric acid, HNO_3: 6N

strontium standard solution, $Sr(NO_3)_2$: volumetrically diluted from the strontium carrier solution to the approximate concentration of strontium in the sample (*e.g.*, the strontium carrier in the ion exchange method is diluted 1:50)

Apparatus

Beckman DU Spectrophotometer: line-operated, equipped with flame attachment, spectral energy recording attachment, photomultiplier, Sargent SR recorder, and atomizer-burner

Procedure

[Note: Directions for operating the flame spectrophotometer are given in the Operating Manual which comes with the instrument.]

1. Dissolve the strontium oxalate precipitate, after it has been counted, in 1 ml of 6N HNO_3. Using distilled water, quantitatively transfer the solution to a 25-ml volumetric flask, and dilute to volume.
2. Fill a 5-ml beaker with the strontium standard solution.
3. Atomize the solution into the flame, and adjust the recorder response so that the recorder reading is at approximately half scale.
4. Fill a 5-ml beaker with distilled water.
5. Atomize the water, and record the response as the background reading.
6. Fill a 5-ml beaker with the sample solution.
7. Atomize the sample solution into the flame, and record the response as the sample reading.

Calculation

$$\text{strontium carrier recovery (\%)} = \frac{A\ (B - C)}{(D - C)} \times 100$$

where A = dilution factor

[when used in conjunction with the ion-exchange procedures, the factor of 0.5 is obtained from the dilution of the recovered strontium by a factor of 25 and the dilution of the strontium carrier solution by a factor of 50 in making the standard strontium solution]

B = sample reading (from Step 7)

C = background reading from water blank (from Step 5)

D = standard reading (from Step 3)

Before being used in the denominator of equations for calculating strontium activity, the percent strontium carrier recovery must be divided by 100 to yield the fraction of carrier recovered.

Reference

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* PHS Publication No. 999-RH-10, Washington, Department of Health, Education, and Welfare, Public Health Service, Environmental Health Series, Division of Radiological Health (1965)

3.3.2 Calcium

REFERENCE METHOD (Overman)

This method is used as a reference method by all laboratories of the Center as a way to maintaining interlaboratory precision. It is more time-consuming than the other methods described, but is more accurate.

Principle of Method

The milk is ashed in a muffle furnace at 550° C, and the ash is dissolved in hydrochloric acid. Calcium oxalate is precipitated from a weakly acid solution, collected by filtration, and washed with ammonium hydroxide. The precipitate is dissolved in sulfuric acid, the solution is heated to 90° C, and calcium is titrated with potassium permanganate.

Reagents

acetic acid, CH_3COOH: glacial (17N)
ammonium hydroxide, NH_4OH: concentrated (15N), 0.5N
ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 3% w/v
hydrochloric acid, HCl: 3N
methyl red indicator: 0.1% w/v
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2.5% w/v
potassium permanganate, $KMnO_4$: 0.05N standardized
sodium acetate, $NaC_2H_3O_2$: 20% w/v
sulfuric acid, H_2SO_4: 2N

Apparatus

burette
platinum crucible, 100-ml capacity

Procedure

1. Pipette 25.0 ml of milk into a platinum crucible, and add 1 ml of glacial acetic acid.
2. Dry the sample overnight in a drying oven at 110° C.
3. Place the sample in a muffle furnace and slowly increase the temperature

to 550° C. Continue to ash at this temperature for 24 hours.

4. Wet the ash with a few milliliters of distilled water, and dissolve it with 10 ml of 3N HCl by warming and allowing it to stand for 30 minutes.
5. Quantitatively transfer the solution to a 400-ml beaker, washing the crucible with distilled water. Dilute the solution in the beaker to approximately 50 ml. Prepare a blank by substituting distilled water for the dissolved milk ash, and run both blank and sample(s) together.
6. Adjust the pH of the solution so that it is just acid to methyl red indicator. Then add 1 ml of 3N HCl.
7. Dilute the solution to about 250 ml with distilled water, and add 20 ml of 2.5% oxalic acid.
8. Cover the beaker with a watch glass, and heat to near boiling on a hot plate. Let the solution digest for 30 minutes.
9. Add 20 ml of 3.0% ammonium oxalate, with stirring, and continue digestion for another 15 minutes.
10. Remove the beaker from the hot plate, slowly add 15 ml of 20% sodium acetate, and allow the solution to stand at room temperature overnight.
11. Collect the calcium oxalate precipitate on a 2.4-cm diameter glass fiber filter in a Gooch crucible (30-ml capacity). Rinse the beaker and wash the precipitate three times with 10-ml portions of 0.5N NH_4OH.
12. Transfer the filter to the beaker in which the oxalate was precipitated, and add 100 ml of water and 100 ml of 2N H_2SO_4. Dissolve any precipitate remaining in the Gooch crucible in 2N H_2SO_4, and wash it into the beaker.
13. Heat the solution to 80-90° C, and titrate with standardized 0.05N $KMnO_4$ to a faint pink color which persists for at least 30 seconds.

Calculation

$$\text{Calcium (g/liter)} = \frac{A \times (B - C) \times D}{E}$$

where A = equivalent weight for calcium (g/eq)

B = volume of $KMnO_4$ used for the sample (ml)

C = volume of $KMnO_4$ used for the blank (ml)

D = normality of $KMnO_4$ (eq/liter)

E = sample volume (ml)

References

Furman, N. H., ed. *Standard Methods of Chemical Analysis, Vol I*, 6th Ed. Princeton, Van Nostrand (1962)

Overman, O. R. *et al. Determination of Calcium in Milk.* Illinois Agricultural Experimental Station Bulletin No. 567 (1953)

PERMANGANATE TITRATION

This method is simple and readily followed by technicians. Two technicians working together can perform approximately 100 analyses per day.

This method is designed for use with the ion-exchange method given in 3.2.3, page 3-19. However, it may be adapted for independent use by merely passing a small aliquot of milk over the cation-exchange resin and eluting with sodium chloride solution.

Principle of Method

Milk is passed through cation- and anion-exchange resin columns. Strontium, barium, and calcium are adsorbed on the cation-exchange resin, then eluted with sodium chloride solution. An aliquot of the cation column eluate is diluted to reduce the high sodium ion concentration. From this diluted aliquot, calcium oxalate is precipitated, dissolved in dilute hydrochloric acid, and the oxalate is titrated with standardized potassium permanganate.

Reagents

ammonium hydroxide, NH_4OH: $6\underline{N}$
ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: $0.03\underline{N}$
anion-exchange resin: Dowex 1-X8 (Cl^- form, 50-100 mesh)
carrier solutions:
  Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
  Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20 mg Sr^{+2} per ml
  Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml
cation-exchange resin: Dowex 50W-X8 (Na^+ form, 50-100 mesh)
citrate solution: $3\underline{N}$ (pH 6.5)
hydrochloric acid, HCl: $6\underline{N}$
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: $1\underline{N}$
potassium permanganate, $KMnO_4$: $0.05\underline{N}$ standardized
sodium chloride, $NaCl$: $4\underline{N}$
sodium oxalate, $Na_2C_2O_4$: National Bureau of Standards, Primary Standard

Apparatus

burette

ion-exchange system: [See description page 3-21 and Figure 3.2-1, page 3-22]

Procedure

1. Follow the ION-EXCHANGE PROCEDURE — TBP Extraction Part A, Steps 1 through 4 and Part B, Step 5.
2. Into a 40-ml glass centrifuge tube, pipette a 20-ml aliquot of the initial eluate collected in Step 5, page 3-26.
3. Dilute the 20-ml aliquot to approximately 30 ml with distilled water.
4. Heat in a hot water bath. Add 10 ml of 1N oxalic acid, and stir. While hot, adjust to pH 3 with 6N NH_4OH (use a pH meter) to precipitate calcium oxalate. Cool slowly to room temperature, centrifuge, and discard the supernate.
5. Thoroughly wash the precipitate and the wall of the centrifuge tube, using not more than 10 ml of 0.03N ammonium oxalate. Centrifuge, and discard the supernatant wash solution.
6. Wash the precipitate with 10 ml of hot distilled water. Cool slowly to room temperature, centrifuge, and discard the supernate. [A stirring rod may be used to agitate the precipitate while it is being washed. It is important to remove all excess oxalic acid from the precipitate.]
7. Dissolve the precipitate in approximately 2.5 ml of 6N HCl with gentle heating.
8. Dilute the acid solution to approximately 10 ml with distilled water. Quantitatively transfer it to a 125-ml Erlenmeyer flask, rinsing the centrifuge tube with water.
9. Add an additional 1 ml of 6N HCl, and adjust the volume of solution to approximately 25 ml with distilled water. Heat to just below boiling.
10. While hot, titrate with standardized 0.05N $KMnO_4$ to the first faint pink endpoint which persists for at least 30 seconds.

Calculation

$$\text{calcium (g/liter)} = \frac{A \times B \times C}{D}$$

where A = volume of $KMnO_4$ solution used for titration (ml)

B = normality of standardized $KMnO_4$ solution (meq/ml) [average of three values from the standardization]

C = milli-equivalent weight of calcium (mg/meq)

D = sample volume (ml)

Since the sample size is 20 ml and the milli-equivalent weight of calcium is 20 mg, the equation reduces to

$$\text{calcium (g/liter)} = A \times B$$

Evaluation of Data

The standard deviation of replicate analyses has been determined to be ±0.02 g/liter.

References

Scott, W. W., ed. "Volumetric determination of calcium". *Standard Methods of Chemical Analysis, Vol I,* 5th Ed., p. 211 (1939)

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

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EDTA TITRATION

Since calcium caseinate is the material actually titrated in this method, only whole milk may be analyzed. The presence of casein also prevents the precipitation of calcium phosphates at the pH of the titration.

Although the procedure is not difficult, some experience is required to judge the subtle color change which indicates the endpoint of the titration.

Principle of Method

An aliquot of milk is diluted with water, hydroxylamine hydrochloride and potassium hydroxide are added, and the resulting solution is titrated with disodium ethylenediamine tetraacetate, using Cal-Red as the indicator.

Reagents

Cal-Red* indicator: dilute (1% w/v)
disodium ethylenediamine tetraacetate [EDTA], $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$: 0.04N
hydroxylamine hydrochloride, $NH_2OH \cdot HCl$: 5% in ethyl alcohol
potassium hydroxide, KOH: 5N

Apparatus

burette

Procedure

1. Pipette 10 ml of milk into a 125-ml Erlenmeyer flask, and dilute with 50 ml of distilled water.
2. Add 5 ml of 5% $NH_2OH \cdot HCl$ and 5 ml of 5N KOH. Mix, and allow to stand for 3 minutes.
3. Add approximately 0.1 grams of Cal-Red indicator, and titrate immediately with 0.04N EDTA. At the endpoint, the solution will change from a lavender color to baby blue.

---

* "Cal-Red Indicator - Dilute" can be obtained from Scientific Service Laboratories, Inc., P. O. Box 175, Dallas, Texas 75221

Calculation

$$\text{calcium (g/liter)} = \frac{A \times B \times C}{D}$$

where A = equivalent weight for calcium (g/eq)
B = volume of EDTA (ml)
C = normality of EDTA (eq/liter)
D = sample volume (ml)

Evaluation of Data

The standard deviation of replicate analyses is ±0.02 g/liter. The results obtained by this method ranged from 0 to 5% higher than those obtained from the REFERENCE METHOD (Overman) (page 3-46).

References

Johns, F. G., D. Moden, E. L. Halker, and A. Bruner. "A rapid determination of calcium in milk". (internal report) U. S. Dept. of Health, Education, and Welfare, Public Health Service, Southwestern Radiological Health Laboratory, Las Vegas (1963)

Schwarzenback, G. *Complexometric Titrations.* New York, Wiley - Interscience Publishers (1957)

3.3.3 Potassium

FLAME PHOTOMETRIC METHOD

This flame photometric method is rapid and accurate for the determination of potassium in any liquid milk sample. The method has been used extensively as a comparison for potassium determinations made by gamma spectrometry.

With the appropriate standards for the flame photometer calibration curve, this method may also be used for sodium, calcium, and magnesium determinations.

Principle of Method

Milk, to which acetic acid has been added, is heated in a water bath until the casein separates. The mixture is centrifuged, filtered, and the filtrate is passed through a column of cation-exchange resin (H^+ form). Potassium, sodium, calcium, and magnesium are quantitatively adsorbed on the resin. These elements are eluted from the resin with hydrochloric acid, and the concentration of potassium in the eluate is determined by flame spectrophotometry.

Reagents

acetic acid, CH_3COOH: glacial (17N)
cation-exchange resin: Dowex 50W-X8 (H^+ form, 50-100 mesh)
hydrochloric acid, HCl: 3.5N, 0.5N
potassium blank solution: 3,500 ppm Na^+, 8,000 ppm Ca^{+2}, and 120 ppm Mg^{+2}
potassium standard solution: 1,000 ppm K^+ in 0.5N HCl

Apparatus

Beckman DU Spectrophotometer: line-operated, equipped with flame attachment, spectral energy recording attachment, photomultiplier, Sargent SR Recorder, and atomizer-burner
glass column with extra-coarse, fritted glass bottom, 30-ml capacity, 1.9-cm diameter, 10.5 cm long

Procedure

1. Fill the 30-ml glass column with 10 ml Dowex 50W-X8 (H^+ form) resin by pouring the resin into the column containing 5 ml distilled water.
2. Measure 60 ml of milk in a graduated cylinder. Using distilled water, wash milk from the cylinder into a graduated 250-ml beaker, and dilute to approximately 100 ml.
3. Add 2 ml of glacial acetic acid, and stir. Heat in a water bath at 80° C for 10 minutes or until casein separates from the milk serum.
4. Dilute the mixture to 150 ml with distilled water. Transfer to a 250-ml centrifuge bottle (do not wash out the beaker). Centrifuge.
5. Decant the supernatant serum into a beaker, and filter it through Whatman No. 541 filter paper to remove small particles of casein which do not settle out with centrifugation. Collect 100 ml of this filtrate in a graduated cylinder. Discard the casein coagulate.
6. Using distilled water, quantitatively transfer the 100-ml sample to a separatory funnel.
7. Attach the separatory funnel to the resin-filled column prepared in Step 1. Let the solution pass over the resin at a flow rate of 4 milliliters per minute (ml/min). Discard the effluent.
8. Wash the resin with 30 ml of distilled water, discarding the wash water.
9. Attach to the top of the column a separatory funnel containing 75 ml of 3.5$\underline{N}$ HCl. Let acid flow through the resin at a flow rate of 2 ml/min. Discard the first 3 ml of effluent. Collect the next 50 ml of eluate in a volumetric flask.
10. Allow the remaining 3.5$\underline{N}$ HCl to flow through the column to recharge the resin. Discard the effluent. Wash the resin with 50 ml of distilled water, and discard the effluent water.
11. Pipette into a 100-ml volumetric flask 3 ml of the 50-ml volume of eluate collected in Step 9. Dilute to volume with 0.5N HCl.
12. Use this 3:100 dilution to determine the concentration of potassium.

Follow directions given in the instruction manual which accompanies the instrument to operate the flame spectrophotometer.

Preparation of Calibration Curve

1. Pipette into six 200-ml volumetric flasks, in sequence, 3.0, 4.0, 5.0,

6.0, 7.0, and 8.0 ml of the potassium standard solution. The contents of these flasks will represent 15, 20, 25, 30, 35, and 40 parts per million (ppm) potassium, respectively.

2. Pipette into each of the volumetric flasks 2 ml of the potassium blank solution.
3. Dilute the contents of each flask to volume with 0.5N HCl, and mix thoroughly.
4. Fill a 5-ml beaker with distilled water, and atomize as described in the instruction manual. Record the response to determine the background or blank reading.
5. Fill 5-ml beakers with each of the potassium standard solutions. Atomize the first standard solution, and record the response. Then atomize a distilled water blank, and again record the response. In this manner, continue to atomize a standard solution followed by a water blank until all six standard solutions have been run.
6. Subtract each background response reading from its corresponding standard response reading. Plot the six net readings on linear graph paper with potassium ion concentration (ppm) as the abcissa, and net response reading as the ordinate.

Flame Determination of Sample

1. Fill a 5-ml beaker with distilled water, and atomize. Record the response as the background reading.
2. Fill a 5-ml beaker with the sample solution. Atomize, and record the response as the sample reading.

Calculation

1. Subtract the background response from the sample response obtained in the Flame Determination, and compare to the calibration curve.
2. Read the ppm of potassium contained in the sample from the calibration curve.
3. Multiply ppm by 0.0416 g/liter-ppm to obtain grams of potassium per liter of milk. This conversion factor accounts for the dilutions of the sample and for the relationship of ppm to grams per liter.

Evaluation of Data

Duplicate sample analyses have a standard deviation of ±0.05 grams per liter. The precision of this method compares favorably with that of the determination of potassium by gamma spectrometry (page 3-58).

References

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

Wenner, V. R. "Rapid determination of milk salts and ions. I. Determination of sodium, potassium, magnesium, and calcium by flame spectrophotometry". *J Dairy Sci 41*:761-768 (1958)

GAMMA SPECTROMETRY

Potassium 40 occurs as a constant proportion (0.0119%) of natural potassium. Therefore, stable potassium can be determined by analysis of potassium 40 by gamma spectrometry. The only requirement is that the potassium content be high enough, or the sample size large enough, to meet the sensitivity level of the detector system.

A discussion of gamma pulse height analysis of potassium 40 for the determination of potassium is given in SECTION 1. INSTRUMENTATION. Refer to parts 1.1.3 and 1.1.4.

Reference

Kahn, B., G. K. Murthy, C. Porter, G. R. Hagee, G. J. Karches, and A. S. Goldin. *Rapid Methods for Estimating Fission Product Concentrations in Milk.* Public Health Service Publication No. 999-R-2, Environmental Health Series, Radiological Health (1963)

SECTION 4.

FOOD

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SECTION 4. FOOD

4.0 INTRODUCTION

Because ingestion is an important route by which radionuclides enter the body and contribute to the human radiation exposure, radioassay of food is a major part of the radiation surveillance activities of the National Center for Radiological Health. Its food surveillance program is centered around analysis of dietary samples rather than individual food items, except milk, because the radioanalysis of composite food samples provides a better indication of the amount of radionuclides ingested by the segments of the U. S. population sampled. Radioassay of milk is discussed separately in SECTION 3.

Radioassay of food samples collected by the Center is designed around three basic procedures: 1) gamma spectrometry, 2) chemical separation of radiostrontium from yttrium with subsequent determination of strontium 90 and strontium 89, and 3) radium 226 analysis. As long as no interfering radionuclides are present other than naturally occurring radioactive potassium (^{40}K), the minimum detectable concentration of iodine 131, cesium 137, and barium 140 by gamma spectrometry is 10 picocuries per kilogram of sample. Five picocuries of strontium 89, 1 picocurie of strontium 90, and 1 picocurie of radium 226 per kilogram of sample are the minimum concentrations detected by the radiochemical procedures.

Stable calcium in food samples is measured because calcium compounds may influence the uptake of bone-seeking radionuclides such as radiostrontium. Stable potassium is measured as it provides a handy reference point for the analysis. An unusual concentration of potassium 40 and therefore of stable potassium indicates something is wrong with the analysis, with the sample, or with both.

The procedures in this Section are those used by the Center's laboratories to analyze stable elements and radionuclides on a one-time basis. They allow a high level of precision and are not performed rapidly or by untrained technicians. They cannot be used effectively for emergency situations where a rapid estimate of the radionuclide content would be required.

4.1 PREPARATION OF SAMPLES

Preparation of food samples for analysis of radionuclides involves three major operations. Each is essential to obtain results which are valid, accurate, and precise.

The first is to insure that the food sample represents the edible portion or the portion actually consumed. Inedible material such as bone, apple cores, nut shells, and egg shells should not ordinarily be included as part of the sample. To be valid as a dietary sample of a meal, the food for the entire meal should be prepared and "served" in reasonable portions or multiples thereof. Any convenient amount of a single food item can be sampled and the radionuclide content reported on a weight or volume basis.

The second operation in food sample preparation is to make the sample homogeneous so that aliquots will be identical in composition. This is best accomplished by blending or homogenizing using commercial blenders or specially constructed homogenizers, depending on the sample load and typical sample size.

The third operation is to put the homogeneous sample into solution. It is accomplished by ashing in a muffle furnace, digesting in acid, by fusing, or by a combination of these. The volatilization temperatures of the radioactive elements to be analyzed influences the choice of procedure. Volatile gamma emitters such as radioiodine and cesium isotopes can be measured in the undissolved homogenate by gamma spectrometry. If a radioelement volatile at dry ashing temperatures cannot be determined by gamma spectrometry, it can be analyzed chemically after the sample has been dissolved by acid digestion as described in 7.2 of SECTION 7.

Food samples should be packaged in waterproof containers, frozen during storage, and thawed prior to analysis. Food samples collected in the Institutional Total Diet Sampling Program of the National Center for Radiological Health are frozen and packed in dry ice for shipment to the Center's laboratories. This treatment obviates the need for adding a preservative to the samples.

Institutional diet samples usually range from 6 to 16 liters in volume and from 8 to 20 kilograms in weight. Convenient sample and aliquot size for individual food items or composites of known constituents can be determined from Table 4.1-1.(1)

Reference

1. Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

Table 4.1-1 Required amount and approximate ash content of various sample media

MEDIUM		REQUIRED AMOUNT* (kg)	APPROXIMATE ASH CONTENT (%)
Apples		13.0	0.3
Bananas		4.0	0.9
Beans	(green, snap)	5.5	0.6
	(kidney, dry)	2.5	1.6
	(large lima, dry)	2.5	1.6
	(pinto, dry)	2.5	1.8
Beef	(meat)	5.0	0.7
Bones		0.2	18.0
Bread		1.7	2.0
Cabbage		7.0	0.5
Carrots		3.5	1.1
Celery		4.5	0.8
Cereals	(All Bran)	0.5	8.2
	(Cheerios)	1.0	4.5
	(Corn Flakes)	1.5	3.1
	(Grape-Nuts)	1.5	2.6
	(Rice Krispies)	1.5	3.1
	(Shredded Wheat)	2.5	1.4
	(Special "K")	1.5	3.0
	(Wheaties)	1.0	4.8
Coffee	(instant)	0.4	12.0
	(regular, brewed)	1.8	0.2
Crab	(whole)	0.5	14.5
Diet Foods	(composite)	3.5	1.0
Eggplant		5.0	0.8
Eggs		5.0	0.7
Fish	(whole)	0.5	6.5
	(edible, red snapper)	2.0	1.8
Grass	(dry)	1.0	5.5
	(green)	2.0	2.0
Lettuce		7.0	0.5
Milk	(evaporated)	2.5	1.6
	(fresh)	5.0	0.7
Oleomargarine		1.6	2.3
Oranges		9.0	0.4

(Continued)

Table 4.1-1 Continued

MEDIUM		REQUIRED AMOUNT* (kg)	APPROXIMATE ASH CONTENT (%)
Oysters	(meat)	0.5	6.0
Pork	(meat)	5.0	0.8
Potatoes	(fresh)	4.0	1.0
Pumpkins		8.5	0.4
Rice	(white)	7.0	0.5
Rutabagas		6.0	0.6
Shrimp	(whole)	1.0	4.5
Silt		1.0	variable
Squash		5.0	0.7
Tomatoes		4.5	0.8
Watermelon		13.0	0.3

* In order to have sufficient ash for the chemical procedures listed in this manual.

4.1.1 Blending

Several methods of sample blending may be used to homogenize liquid, semi-liquid, and solid samples of food, excluding inedible, hard and resistant parts such as bones and skin. One of the three procedures described here can be applied to large or small numbers of samples or to samples of large or small volume. Because they differ primarily in the type of apparatus employed, choice of procedure will be dictated by the sample load, sample size, availability of funds and equipment, and personal preference of the analyst.

Principle of Method

The food sample is weighed and thoroughly blended in a homogenizing apparatus until the sample becomes a homogeneous slurry. Portions of the slurry are measured into appropriate containers for analysis by gamma spectrometry and/or for ashing prior to radiochemical analysis.

PROCEDURE A

Reagents

none

Apparatus

evaporating dish
laboratory balance
Marinelli-type beaker, 3.5-liter capacity
stainless steel electric food blender, 1-gallon capacity

Procedure

1. Weigh the total sample, and homogenize it in a 1-gallon capacity blender. After the sample appears to be a slurry, blend it for 3 minutes longer.
2. Measure 3.5-liters of the homogenized sample into a tared Marinelli type beaker and determine the aliquot weight. This portion is counted

for gamma activity in a gamma scintillation spectrometer (SECTION 1). After the blended sample is counted for gamma activity it may be transferred to a pre-weighed evaporating dish to be ashed in preparation for further analysis.

PROCEDURE B

Reagents

none

Apparatus

Corning Ware dish, 2-quart capacity
electric blender
laboratory balance, 10-kg capacity
Marinelli-type beaker, 3.5-liter capacity
stainless steel container, 10-gallon capacity

Procedure

1. Weigh the total sample and transfer the solid portion to a 10-gallon stainless steel container. Blend for 20 minutes with an electric blender. Add the liquid portion and blend for 10 minutes longer.
2. Transfer 3.5 liters of blended sample into a Marinelli-type beaker. This portion is counted for gamma activity in a gamma scintillation spectrometer (SECTION 1), after which it may be transferred to pre-weighed Corning Ware dishes to be ashed in preparation for further analysis.

PROCEDURE C

Reagents

none

Apparatus

Environmental Residue Processing apparatus, Model B (ERP-B) See Figure 4.1.1-1
laboratory balance, 10-kg capacity
Marinelli-type beaker, 3.5-liter capacity

Procedure

1. Weigh the sample and container(s). If the liquid and solid portions of the sample are in separate containers, first pour the liquid portion into the disposal unit of the ERP-B apparatus (Figure 4.1.1-1) and turn the control switch to the "operate" position to start the disposal unit and pump. Weigh the emptied liquid container. Then add the solids through the disposal unit, removing all hard, inedible, or other waste parts from the sample and returning them to the container. Weigh the empty container(s) and any waste parts to determine total weight of the edible portion.

   [Note: Operate the circulating pump only when there is water or a sample in the reservoir. The rubber impeller will wear excessively if operated when the reservoir is dry.]
2. Recirculate the sample for 10 minutes until it has the consistency of a slurry. A fail-safe circuit (Figure 4.1.1-2) in the pump is designed to turn off the pump in case the thermal overload breaker on the disposal unit breaks the circuit. When this happens, turn off the control switch. If the disposal blade is jammed, free it and push the overload button on the outside of the disposal unit. This will restart the apparatus.
3. Using the sample valve attached to the reservoir (Figure 4.1.1-1), transfer 3.5 liters of the blended slurry to a tared Marinelli-type beaker. Transfer a 2000-ml portion of the slurry into a graduated cylinder. Weigh the beaker and slurry prior to counting the gamma activity of the sample in a gamma scintillation spectrometer (SECTION 1). Save the 2000-ml portion for ashing.
4. To clean the apparatus, add and circulate tap water through the disposal unit and open the sewer connecting valve. This dilutes the remaining slurry and pumps it into the sewer.
5. Close the sewer connection. Continue adding water and also add a small amount of detergent to the disposal unit. When the reservoir fills, open

the sewer connection and rinse with water until all suds disappear.

6. Throw the control switch to "pump" position to operate the pump and drain the unit. Close the sewer connection and turn off the control switch. A small quantity of water will remain in the lower part of the apparatus. Before the next operation, remove the drain plug, let this water drain into a beaker, and discard it.

Reference

Radiochemistry Laboratory Program — Southwestern Radiological Health Laboratory. *Analytical Methods of the Southwestern Radiological Health Laboratory.* Las Vegas, U. S. Department of Health, Education, and Welafer, Public Health Service, Division of Radiological Health (internal report 1963)

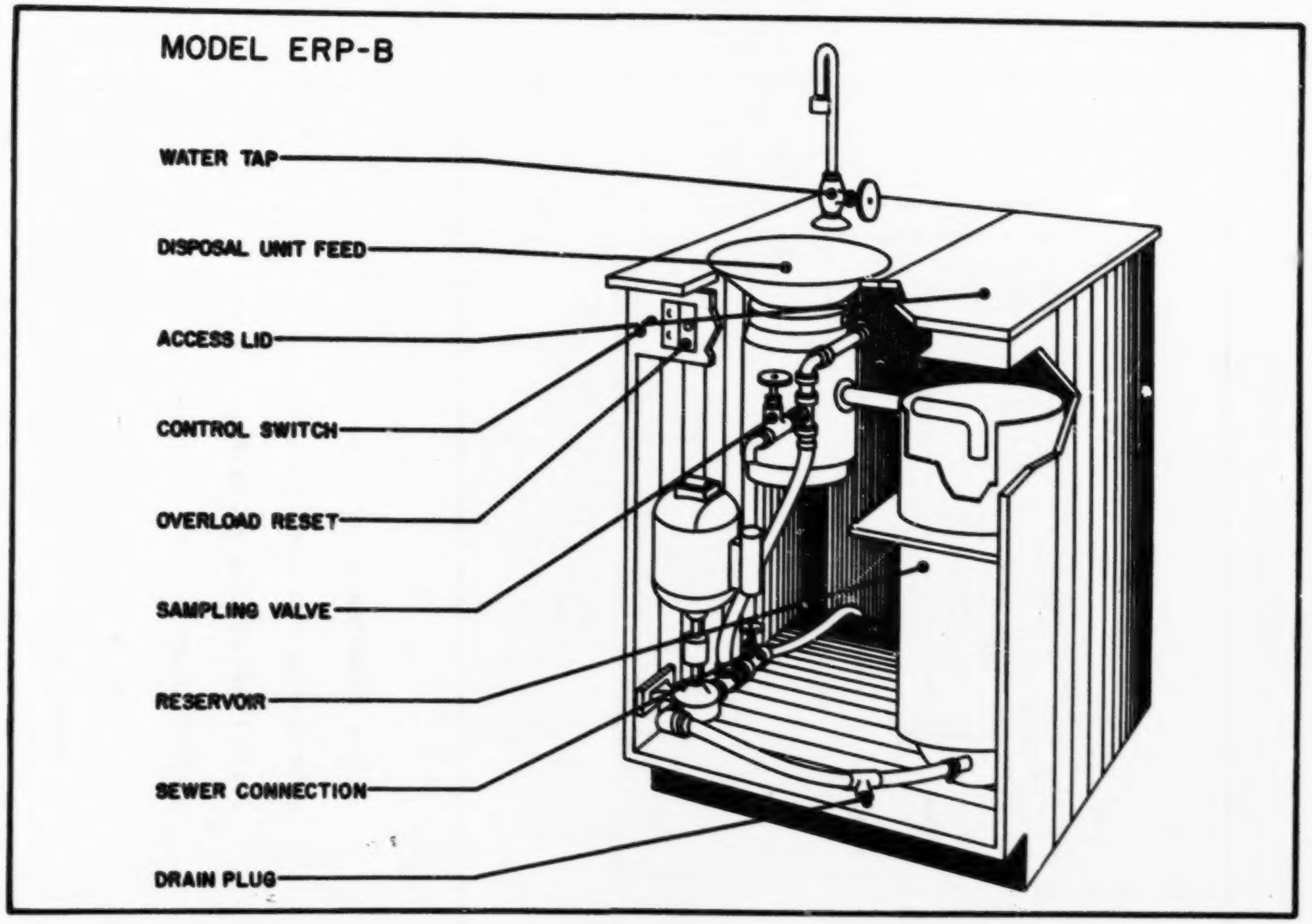
MODEL ERP-B
WATER TAP
DISPOSAL UNIT FEED
ACCESS LID
CONTROL SWITCH
OVERLOAD RESET
SAMPLING VALVE
RESERVOIR
SEWER CONNECTION
DRAIN PLUG

Figure 4.1.1-1 Environmental Residue Processing apparatus, Model B

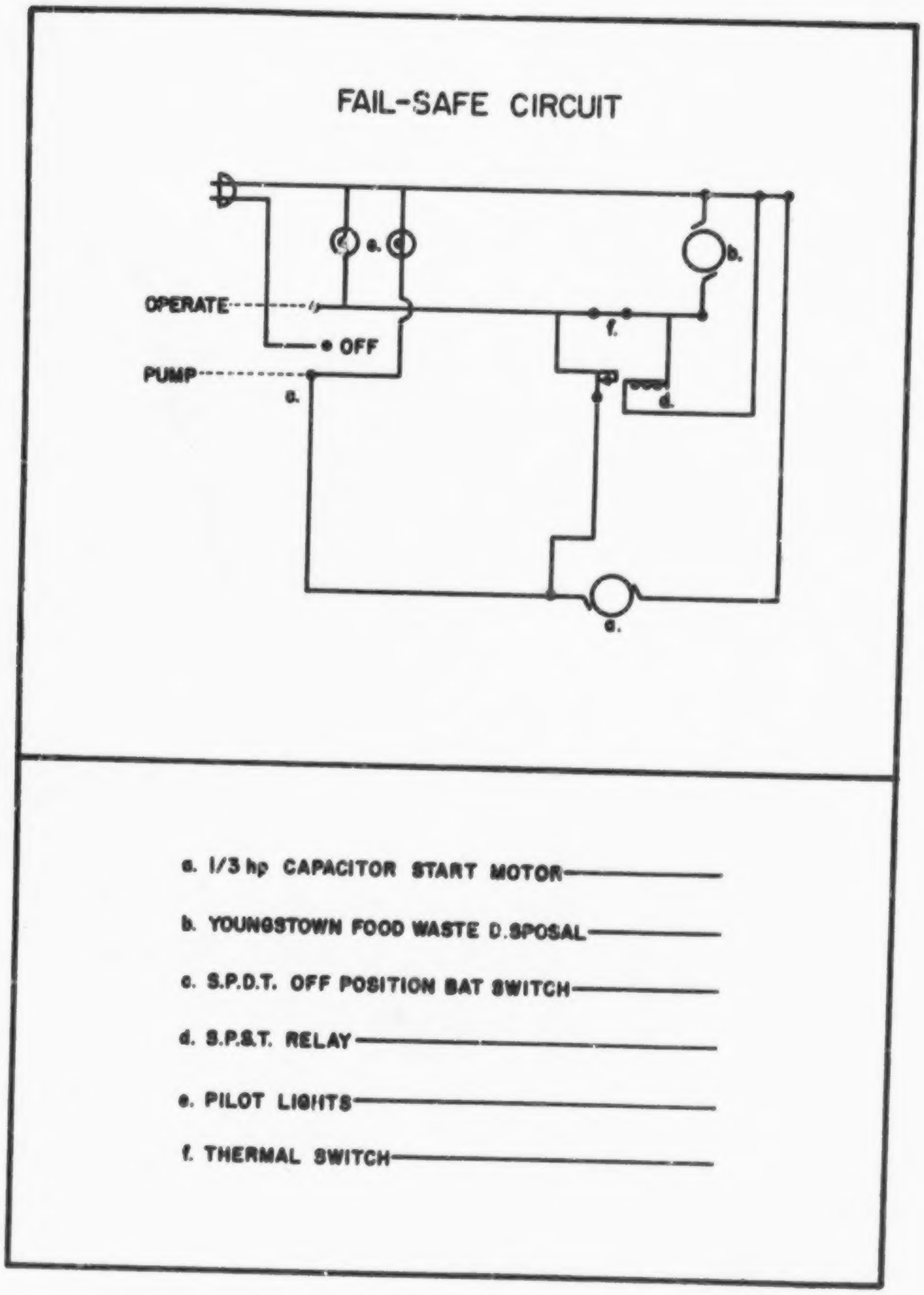
FAIL-SAFE CIRCUIT
e.
b.
OPERATE
OFF
PUMP
c.
f.
d.
a.
a. 1/3 hp CAPACITOR START MOTOR
b. YOUNGSTOWN FOOD WASTE DISPOSAL
c. S.P.D.T. OFF POSITION BAT SWITCH
d. S.P.S.T. RELAY
e. PILOT LIGHTS
f. THERMAL SWITCH

Figure 4.1.1-2 Wiring diagram for Environmental Residue Processing apparatus, Model B

4.1.2 Ashing

Three similar procedures for ashing food samples are given here. They are used in the Center's laboratories in connection with the three methods of blending described in 4.1.1 and any one of them can be applied to a blended dietary sample or a raw, cooked, or unhomogenized food item, although special care must be taken in ashing intact fatty substances. If not homogenized, most samples should be cut into small pieces before being ashed. In each precedure, ambient temperature is progressively increased to reduce the consistency of the sample to that of a coarse gravel.

Muffle furnaces are the only major laboratory equipment needed, and the number of samples that can be ashed per day depends primarily on the number and capacity of furnaces available. PROCEDURE A requires the least muffle furnace time and PROCEDURE C the most. The minimum time required to ash a single sample is a little over three days; however, the sample needs to be watched or handled only occasionally.

Principle of Method

The blended sample is dried and then ashed in a muffle furnace by progressively increasing the furnace temperature to 500° to 600° C. The ash is then cooled, weighed, pulverized or mixed by a similar method, and divided into portions needed for analysis.

PROCEDURE A

Reagents

none

Apparatus

Corning Ware dish
electric drying oven
evaporating dish
gas oven

muffle furnace
plastic container

Procedure

1. Transfer a suitable portion (see Table 4.1-1) of a blended sample to a tared Corning Ware dish and obtain the aliquot weight. Dry the sample in an electric drying oven at 115° C for 48 hours.
2. Transfer the sample to a gas oven and char for 4 hours at 250° C. Then raise the temperature to 315° C for an additional 4 hours. Then raise the temperature to 480° C and char for 8 hours more. Remove the sample, and cool it.
3. Transfer the cooled, charred ash to an evaporating dish and place it in a muffle furnace. Raise the temperature to 550° to 600° C and ash for 16 hours.
4. Cool, weigh, and then grind the ash to a fine powder using a mortar and pestle.
5. Transfer the powdered ash to a plastic container from which portions can be removed for chemical analysis.

PROCEDURE B

Reagents

none

Apparatus

Corning Ware dish
drying oven
muffle furnace
plastic container

Procedure

1. Transfer a suitable portion (see Table 4.1-1) of a blended sample to a tared Corning Ware dish and obtain the aliquot weight.
2. Dry the sample in an oven at 100° to 120° C for 48 hours.

3. Transfer the sample to a muffle furnace, and raise the temperature slowly from 200° to 550° C. Keep the temperature of the furnace at 550° C and ash the sample for 48 hours.
4. Cool, weigh, and then grind the ash to a fine powder using a mortar and pestle.
5. Transfer the powdered ash to a plastic container from which portions can be removed for chemical analysis.

PROCEDURE C

Reagents

none

Apparatus

muffle furnace
porcelain evaporating dish, 2-quart capacity

Procedure

1. Transfer a suitable portion (see Table 4.1-1) of a blended sample to a tared porcelain evaporating dish and obtain the aliquot weight.
2. Place the sample in a vented muffle furnace, and dry overnight at 150° C.
3. Carefully raise the temperature in small increments to 600° C. The increase must be gradual enough to prevent the sample from creeping or splattering. Keep the temperature of the muffle furnace at 600° C and ash the sample for 48 hours.
4. Cool, weigh, and then grind the ash to a fine powder using a mortar and pestle.
5. Transfer the ash to a plastic container from which aliquots may be removed for chemical analysis.

4.1.3 Fusion

If a food sample contains a high concentration of silica, it may be necessary to perform a sodium carbonate fusion on the ash in order to dissolve it.

SODIUM CARBONATE FUSION

Principle of Method

Barium and strontium carriers are added to an aliquot of food ash and the mixture is fused with sodium hydroxide and sodium carbonate. The melt is taken up in distilled water, washed, and treated with sodium carbonate to yield a precipitate of alkaline earth carbonates. The carbonate precipitate can be analyzed for strontium 89, strontium 90 and barium 140.

Reagents

carrier solutions:

Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml

Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20 mg Sr^{+2} per ml

sodium carbonate, Na_2CO_3: anhydrous granules or powder, 3N, 0.1N

sodium hydroxide, NaOH: pellets

Apparatus

long-handled tongs, nickel-tipped
nickel crucible, 250-ml capacity
nickel spatula

Procedure

1. Weigh a 10-gram or smaller portion of food ash into a 250-ml nickel crucible. Record the weight.
   [Note: Sample size depends on the silica content of the ash.]
2. Pipet 1.0 ml of strontium carrier solution and 1.0 ml of barium carrier solution (or an amount of carrier suitable to the analysis to be made) into the crucible. Mix thoroughly with a nickel spatula.

3. To this mixture add 50 grams of sodium hydroxide pellets, or 5 grams for each gram of ash, and mix thoroughly.
4. Fuse over a blast burner for 20-30 minutes. Then slowly stir in 5 grams of anhydrous sodium carbonate, or 0.5 gram for each gram of ash. Continue to heat the clear red melt for 20-30 minutes.
5. Using long-handled, nickel-tipped tongs, remove the crucible from the flame and very cautiously cool it in a cold-water bath. Take up the cooled melt in about 200 ml of hot distilled water and disintegrate it by gentle boiling.
6. Using distilled water, transfer the mixture to a 250-ml centrifuge bottle. Centrifuge, and discard the supernatant liquid.
7. To the residue add 40 ml 3N Na_2CO_3 as a wash. Heat for 10 minutes on a hot plate. Centrifuge, and discard the supernate.
8. Repeat Step 7 to put the precipitate in a form suitable for further analysis.

4.2 DETERMINATION OF RADIOACTIVITY

4.2.1 Strontium 90

HDEHP EXTRACTION METHOD

This di(2-ethyl-hexyl)phosphoric acid extraction method may be used to determine strontium 90 in any sample which has been reduced to an ash. The extraction is specific for yttrium, so total radiostrontium and strontium 89 are not determined.

Because the method is carrier free, a "weightless" sample is counted, and a larger sample of ash can be analyzed. This makes the method particularly useful for samples in which the concentration of strontium 90 is very low.

Laboratory and equipment requirements are modest, and a large number of samples can be handled without sacrificing precision. Eight days are required to complete the procedure, but few man-hours are needed because constant attention to the sample is not necessary.

Principle of Method

A weighed portion of an ashed sample is dissolved in warm, dilute hydrochloric acid, and the solution is filtered. The pH of the filtrate is adjusted to 1.4, and yttrium is removed by extraction into di(2-ethylhexyl)phosphoric acid [HDEHP] in toluene. The acid solution containing the strontium is stored for one to two weeks for yttrium 90 to grow in.

At the end of the storage period, yttrium 90 is extracted from the acid solution into HDEHP in toluene. The organic solution is scrubbed with hydrochloric acid, and yttrium 90 is back-extracted into nitric acid. This nitric acid solution is reduced in volume by evaporation, transferred to a counting dish, and evaporated to dryness. The nitrate residue is counted for the beta activity of yttrium 90 from which the strontium 90 activity is calculated.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N)

di(2-ethyl-hexyl)phosphoric acid [HDEHP]: 20% v/v in toluene, 5% v/v in toluene

hydrochloric acid, HCl: 6N, 0.06N adjusted to pH 1.4

nitric acid, HNO_3: fuming (90%), concentrated (16N), 3N

Apparatus

analytical balance
low-background beta counter
pH meter

Procedure

1. On an analytical balance, weigh a sufficient portion of the ashed sample into a 1-liter beaker. Add 300 ml 6N HCl, and warm the beaker to dissolve the ash. Cool, and filter the solution through Whatman No. 2 filter paper.
2. Evaporate the filtrate to 100 ml. Adjust the pH to exactly 1.4 using 16N HCl or 15N NH_4OH and a pH meter. Quantitatively transfer the solution to a separatory funnel using pH 1.4 HCl solution to effect the transfer. The sample solution must be exactly pH 1.4 at the time of extraction.
3. To the funnel, add a volume of 20% HDEHP in toluene equal to that of the aqueous solution, and extract the yttrium into the organic reagent by shaking for 1 minute. RECORD THE TIME AND DATE AS THE BEGINNING OF YTTRIUM 90 INGROWTH (T_1). Allow the phases to separate for 15 minutes. [Note: The volumes of aqueous and organic phases should be the same throughout the procedure.]
4. Drain the aqueous phase into a clean separatory funnel, and repeat the extraction (Step 3). Phase separation should be as clean as possible, but it is better to leave a few drops of aqueous phase in the organic rather than vice versa.
5. Drain the aqueous phase into a suitable glass bottle, and label it. Discard the organic phase. Store the aqueous solution for 1 to 2 weeks for yttrium 90 to grow in.
6. After a suitable storage period, transfer the sample to a separatory

funnel. Retain the sample container without rinsing.

7. Extract yttrium 90 from the solution by adding an equal volume of 5% HDEHP in toluene and shaking for 1 minute. RECORD THE TIME AND DATE AND THE END OF YTTRIUM 90 INGROWTH (T_2) AND THE BEGINNING OF ITS DECAY. Allow the phases to separate for 15 minutes.
8. Drain the aqueous phase into a suitable beaker and save for Step 12.
9. Wash the organic phase twice with equal volumes of the $0.06\underline{N}$ HCl solution. Add the HCl first to the sample container from Step 6 and then to the organic phase in the funnel in order to effect a quantitative transfer of the sample to the funnel. Combine the washes with the aqueous solution saved in Step 8.
10. Back-extract yttrium 90 from the organic phase twice into equal volumes of $3\underline{N}$ HNO_3. For each extraction, shake for 1 minute and allow the phases to separate for 15 minutes. Collect the aqueous phases in a beaker.
11. Evaporate the combined solution to a small volume. Using $3\underline{N}$ HNO_3, transfer the solution to a stainless steel planchet. Evaporate the solution in the planchet to complete dryness, and count in a low background beta counter to determine the beta activity of yttrium 90. RECORD THE TIME AND DATE OF COUNTING.
12. If the sample is to be analyzed for radium, evaporate the aqueous phase retained from Step 8 to dryness, dissolve the residue in $16\underline{N}$ HNO_3, and evaporate again. This residue can be analyzed for radium 226 by the RADON 222 EMANATION METHOD given in 4.2.4.

Calculation

$$\text{strontium 90 activity (pCi/gram ash)} = \frac{A}{0.97 \times B \times C \times D \times E}$$

where A = net beta count rate of yttrium 90 (cpm)

B = efficiency for counting yttrium 90 as an yttrium nitrate residue in a stainless steel planchet (cpm/pCi)

C = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from T_1 [Step 3] to T_2 [Step 7]

D = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t

is the time from the second yttrium extraction at T_2 [Step 7] to the time of counting [Step 11]

E = weight of ash analyzed (grams)

0.97 = efficiency of the chemical extraction

Evaluation of Data

Because the efficiency of yttrium extraction cannot be determined in this carrier-free procedure, an experimentally determined efficiency of 97.0% is used as a constant in the calculation of data. The efficiency should be verified periodically.

References

Radiochemistry Laboratory Program — Southwestern Radiological Health Laboratory. *Analytical Methods of the Southwestern Radiological Health Laboratory.* Las Vegas, U. S. Department of Health, Education, and Welfare, Public Health Service, Division of Radiological Health (internal report 1963)

Radiological Safety Division. "Strontium-90", *Analytical Procedures of the Radiological Safety Laboratory, Nevada Test Site* by E. L. Geiger and E. L. Whittaker. Mercury, Nevada, Reynolds Electrical and Engineering Co., Inc. (internal report 1961)

4.2.2 Strontium 89 and Strontium 90

TTA EXTRACTION METHOD

This procedure is applicable to ashed samples of food as well as to the ash of other biological materials except bone, and is identical to the TTA EXTRACTION METHOD given in SECTION 7. OTHER ENVIRONMENTAL SAMPLES, part 7.2.2. SECTION 7 also contains a method for analysis of radiostrontium in bone ash.

About twenty hours are required to analyze one sample in duplicate by the TTA EXTRACTION METHOD, and in a five-day week, an experienced technician can make duplicate analyses of six to eight samples.

NITRIC ACID SEPARATION METHOD

This method may be used to determine the strontium 89 and strontium 90 content of ashed samples of food, bone, or vegetation. Although efficient fume hoods are a necessity, the required equipment and supplies are usually readily available. The procedure takes approximately fifteen days to complete; however, it may be adapted to handle a large number of samples simultaneously and continuously without sacrificing precision.

The procedure has been used routinely in conjunction with the nitric acid separation method for analyzing radiostrontium in milk. The final steps of the two procedures are identical, and food samples may be processed along with the milk samples after the preliminary trichloroacetic acid precipitation steps of the procedure for milk have been completed.

Principle of Method

A weighed portion of an ashed sample is digested in dilute hydrochloric acid, and the solution is filtered to remove insoluble sediment (silicates). After strontium carrier solution and oxalic acid are added, alkaline earths are precipitated as oxalates by adjusting the pH of the solution to 3.0. Following nitration of the precipitate, calcium and strontium nitrates are separated by differences in their solubility. Barium, iron, and rare earths are then removed by scavenging. After a final nitric acid extraction of yttrium, the strontium precipitate is stored for one to two weeks for yttrium 90 to grow in.

After the storage period, strontium is re-precipitated with nitric acid, and yttrium 90 is recovered in the supernatant solution. Both fractions are mounted in planchets and counted in a low-background beta counter. The beta activity of the yttrium fraction is counted to determine the strontium 90 activity. This is subtracted from the beta activity of total radiostrontium detected in the strontium fraction to determine the strontium 89 activity.

Reagents

ammonium acetate buffer: pH 5

ammonium hydroxide, NH_4OH: concentrated (15N), 6N

ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 0.5% w/v bromcresol green indicator: 0.1% w/v in ethyl alcohol

carrier solutions:

Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 7 mg Ba^{+2} per ml

Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 8 mg Sr^{+2} per ml

hydrochloric acid, HCl: 3N

hydrogen peroxide, H_2O_2: 30% solution

nitric acid, HNO_3: fuming (90%), concentrated (16N), 3N, 0.5N

oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: saturated at room temperature

scavenger solution: 20 mg Fe^{+3} per ml, 10 mg each Ce^{+3} and Zr^{+4} per ml, and 5 ml 12N HCl per liter

Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$

Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$

Zr^{+4} as zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$

sodium carbonate, Na_2CO_3: 3N

sodium chromate, Na_2CrO_4: 0.25N

Apparatus

analytical balance

filter stick, medium-porosity

low-background beta counter

muffle furnace

pH meter

Procedure

1. On an analytical balance, weigh an appropriate portion of ashed sample into a 1-liter beaker. Add about 500 ml of 3N HCl, and warm to dissolve the ash. Cool, and filter the solution through a Whatman No. 2 filter into a 2-liter beaker.
2. Using distilled water, dilute the filtrate to 1 liter, add 10 ml of strontium carrier solution, and stir thoroughly. Add 125 ml saturated oxalic acid solution, and mix thoroughly. Using a pH meter standardized at 4.0, adjust the pH of the solution to 3.0 with 15N NH_4OH. Allow the oxalate precipitate to settle for 5 to 6 hours.
3. Aspirate the supernate through a medium-porosity filter stick. Wash the beaker and the precipitate with 0.5% ammonium oxalate solution while continuing to aspirate.

4. Using 16N HNO_3, transfer the precipitate to a 250-ml beaker, and place the filter stick in the beaker. Heat the sample on a hot plate until the precipitate separates from the filter stick. Rinse the stick inside and out with 16N HNO_3, and remove it.
5. Evaporate the solution to near dryness. Add 50 ml 16N HNO_3, and continue to evaporate. Repeat until the nitrate residue is colorless.
6. Using a minimum volume of 16N HNO_3, transfer the residue to a 40-ml centrifuge tube. Cool the residue in a refrigerator overnight. Centrifuge at 1500-1800 rpm for about 10 minutes, and discard the supernate.
7. Dissolve the precipitate in 5 ml 3N HNO_3, and carefully add 10 ml fuming HNO_3. Centrifuge, and discard the supernate.
8. Dissolve the precipitate in 5 ml distilled water. Add 3 drops bromcresol green indicator. Add 6N NH_4OH until the color changes from yellow to blue. Back-titrate with 0.5N HNO_3 until the solution barely turns yellow. Add 5 ml ammonium acetate buffer solution, then 1.0 ml barium carrier solution, and 1 ml 0.25N Na_2CrO_4. Warm until a definite barium chromate precipitate appears. Cool, and filter through a Whatman No. 42 filter into a 250-ml beaker. Wash the precipitate with warm distilled water before discarding it.
9. To the filtrate, add 5 drops of scavenger solution and 5 drops 30% H_2O_2. Warm the solution and add 15N NH_4OH a drop at a time until a precipitate forms. Filter through a Whatman No. 42 filter. Wash the rare earth precipitate with 6N NH_4OH, and discard it.
10. Evaporate the filtrate to approximately 20 ml. Using a minimum volume of 15N NH_4OH, transfer the filtrate to a 40-ml centrifuge tube. Add 2 ml 3N Na_2CO_3. Mix thoroughly, cool, and centrifuge. When completeness of precipitation is verified, discard the supernate.
11. Dissolve the carbonate precipitate in no more than 6 ml of 3N HNO_3. Add 30 ml fuming HNO_3. Cool in a water bath; then centrifuge, and discard the supernate. Repeat this step. Then, RECORD THE TIME AND DATE AS THE BEGINNING OF YTTRIUM 90 INGROWTH (T_1). Store the nitrate precipitate for one to two weeks. If determination of total radiostrontium activity is desired at this time, the beta activity of the nitrate precipitate can be counted.
12. Pipet 6.0 ml of water into a 40-ml centrifuge tube for use as a volume

standard for the following steps.

13. After a suitable ingrowth period, dissolve the strontium nitrate precipitate in the centrifuge tube, using no more than 6 ml 3N HNO$_3$.

14. Add 30 ml fuming HNO$_3$ to the centrifuge tube, and cool in a water bath. RECORD THE TIME AND DATE AS THE END OF YTTRIUM 90 INGROWTH (T$_2$).

15. Centrifuge, and decant the supernatant solution into a 250-ml beaker.

16. Dissolve the residue in the tube in 6 ml distilled water. Repeat Steps 14 and 15, and combine the supernatant solutions.

17. Evaporate the combined solutions to a small volume. Transfer the concentrate to a heat-proof counting dish, using 3N HNO$_3$ to wash the beaker. Evaporate to absolute dryness. Count the beta activity of yttrium 90 in a low-background beta counter. RECORD THE DATE AND TIME OF COUNTING (T$_3$).

18. With distilled water, transfer the precipitate in the centrifuge tube to a tared heat-proof counting dish. Evaporate to dryness, and weigh the residue in order to determine the self-absorption correction factor for beta counting. Then count the beta activity of the residue in a low-background beta counter to determine the total radiostrontium activity. [Note: Be sure that the residue is absolutely dry. To remove all moisture, the planchet can be heated in a muffle furnace at 400° C for 30 minutes, or flamed over a burner.]

19. Using 3N HNO$_3$, transfer the precipitate from the counting dish to a 250-ml volumetric flask, and determine the strontium carrier recovery by flame spectrophotometry (4.3.1).

Calculations

$$\text{strontium 90 activity (pCi/gram of ash)} = \frac{A}{B \times C \times D \times E \times F}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of strontium carrier [Step 19]

C = efficiency for counting yttrium 90 as yttrium nitrate (cpm/pCi)

D = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from the end of the ingrowth period [T$_2$] to the time of counting [T$_3$]

E = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from the first separation of strontium and yttrium $[T_1]$ to the separation at the end of the ingrowth period $[T_2]$

F = weight of ash (grams)

$$\text{strontium 89 activity (pCi/gram of ash)} = \frac{1}{A \times B}\left[\frac{C}{D \times E} - F(G{\times}H + I{\times}J)\right]$$

where A = efficiency for counting strontium 89 as strontium nitrate (cpm/pCi)

B = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting $[T_3]$

C = net beta count rate of total radiostrontium (cpm)

D = recovery of strontium carrier [Step 19]

E = weight of ash (grams)

F = strontium 90 activity (pCi/gram of ash)

G = correction factor for self-absorption of total radiostrontium as strontium nitrate, obtained by comparing the density thickness (mg/cm^2) with a self-absorption calibration curve

H = efficiency for counting strontium 90 as strontium nitrate (cpm/pCi)

I = efficiency for counting yttrium 90 as yttrium nitrate (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from decantation of the acid solution of yttrium $[T_1]$ to the separation of yttrium from strontium at the end of the ingrowth period $[T_2]$

Evaluation of Data

The reproducibility obtained with this procedure has not been determined statistically. However, the analytical agreement between this method and other methods used by the Center's laboratories is well within ±5%.

4.2.3 Strontium 89, Strontium 90, and Barium 140

TBP EXTRACTION METHOD

The tributyl phosphate extraction method may be used to determine the activity of strontium 89, strontium 90, and barium 140 in any sample which has been ashed and fused with sodium carbonate. The extraction into tributyl phosphate provides a pure yttrium separation and using a fused sample enlarges the variety of sample types which may be handled.

The method is not difficult to perform and does not require extensive laboratory facilities, but efficient fume hoods and reasonable caution must be used for the nitric acid steps. The total time required to complete this analysis is approximately one and one-half weeks, although only 20 man-hours are needed to analyze eight samples.

Principle of Method

A portion of ashed sample to which strontium and barium carriers have been added is fused with sodium carbonate and treated to yield a precipitate of alkaline earth carbonates. The carbonates are converted to nitrates which are scavenged by precipitating the mixed rare earth hydroxides.

Barium is precipitated as the chromate, purified as the chloride, and counted to determine the beta activity of barium 140.

Strontium is precipitated as the nitrate to separate it from yttrium, and is stored to allow yttrium 90 to grow in. After storage, strontium is reprecipitated as the nitrate from concentrated nitric acid in the presence of yttrium carrier. Strontium nitrate is purified by reprecipitation as the nitrate. It is then converted to strontium carbonate, which is weighed and counted for the beta activity of total radiostrontium.

Yttrium in the supernatant solution is extracted into tributyl phosphate, back-extracted into dilute nitric acid, and precipitated as yttrium oxalate, which is weighed and counted for the beta activity of yttrium 90.

Strontium 90 activity is computed from the yttrium 90 activity, and strontium 89 activity is computed as the difference between total radiostrontium activity and that of strontium 90.

Reagents

ammonium acetate buffer: pH 5
ammonium hydroxide, NH_4OH: concentrated (15N), 6N
ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 1N
carrier solution:
  Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml
diethyl ether, $(C_2H_5)_2O$: anhydrous
ethyl alcohol, C_2H_5OH: absolute (100%), 95%
hydrochloric acid, HCl: concentrated (12N), 6N
hydrochloric acid—diethyl ether, HCl—$(C_2H_5)_2O$: 5:1 solution
nitric acid, HNO_3: fuming (90%), 14N, 8N, 6N, 0.1N
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N
scavenger solution: 10 mg each Ce^{+3}, Fe^{+3}, and Zr^{+4} per ml
  Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$
  Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$
  Zr^{+4} as zirconium nitrate, $Zr(NO_3)_4 \cdot 5H_2O$
sodium carbonate, Na_2CO_3: 3N, 0.1N
sodium chromate, Na_2CrO_4: 3N
tri-*n*-butyl phosphate [TBP], $(C_4H_9)_3PO_4$: pre-equilibrated with 14N HNO_3

Apparatus

analytical balance
analytical oven
low-background beta counter
Millipore Type OH membrane filter, 1.5-μ pore size, 2.5-cm diameter
pH meter
suction-filtration apparatus: Millipore Pyrex Hydrosol Microanalysis filter holder, or equivalent

Procedure

1. In a minimum volume of 6N HCl, dissolve the carbonate precipitate obtained by the sodium carbonate fusion described in 4.1.3. Heat to boiling on a hot plate to dissolve the precipitate and expel carbon dioxide. Adjust the solution to pH 3 with 6N NH_4OH. Centrifuge, and decant the supernate into a 40-ml centrifuge tube.
2. Dissolve the precipitate in a minimum volume of 6N HCl. Warm the

solution gently for a few seconds, and bring the pH to 3 with 6N NH_4OH. Centrifuge, and combine the supernate with that from Step 1. If the volume of the combined supernates will be too large, use a second 40-ml centrifuge tube.

3. Repeat Step 2, and discard the precipitate.
4. To precipitate the alkaline earths, add 10 to 15 ml 3N Na_2CO_3 to the supernate obtained from Steps 1, 2, and 3. Digest the carbonate precipitate in a hot water bath for about 30 minutes; then centrifuge. When completeness of precipitation is verified (add a few drops of 3N Na_2CO_3), discard the supernate. Completely dry the precipitate in an oven at 110° C (about 3 hours).
5. Cool the precipitate, and dissolve it in approximately 10 ml 6N HNO_3. Hasten solution by warming and stirring occasionally. To the solution, carefully add a sufficient volume of fuming HNO_3 to obtain a 70% nitric acid concentration (see Table 3.2-1, part 3.2.3). Cool in an ice bath for 5 minutes. Centrifuge, and discard the supernate.
6. Combine (if necessary), and dissolve the nitrate precipitate in about 20 ml distilled water. Add 1 ml of scavenger solution. Adjust the pH of the mixture to 7 with 6N NH_4OH. Heat, stir, and filter through a Whatman No. 541 filter. Discard the mixed hydroxide precipitate.
7. To the filtrate, add 5 ml ammonium acetate buffer. Check the pH with universal pH paper. If necessary, add more buffer solution to bring the pH to 5.
8. To precipitate barium chromate, heat the solution in a water bath, and add 1 ml 3N Na_2CrO_4 a drop at a time while stirring. Centrifuge, and decant the supernate into a 40-ml centrifuge tube.
9. If no barium 140 analysis is needed, omit Steps 9 through 14. Otherwise, add approximately 5 ml 12N HCl to the barium chromate precipitate. Heat in a water bath until the yellow barium chromate [$BaCrO_4$] dissolves and a white, granular barium chloride precipitate [$BaCl_2 \cdot 2H_2O$] remains. At this point the solution will have a greenish color from chromic ion [Cr^{+3}].
10. Cool the solution in an ice bath. Add 20 ml of cold HCl-diethyl ether reagent, and stir. Centrifuge, and decant the supernate. A pure white barium chloride precipitate [$BaCl_2 \cdot 2H_2O$] should remain. If the precipitate still shows any color, repeat the HCl-diethyl ether application. RECORD THE TIME AND DATE OF DECANTATION AS THE BEGINNING OF LANTHANUM 140 INGROWTH (T_1).

11. Weigh a stainless steel planchet and a 2.4-cm diameter Whatman No. 542 filter. Place the filter into the suction-filtration apparatus.
12. Transfer the precipitate onto the filter with three to four 10-ml portions of cold absolute ethyl alcohol.
13. Place the filter with the precipitate in the tared stainless steel planchet. Dry the precipitate in air (∿2 hours) or in an oven at 200° C (∿1 hour) to constant weight. Cool in a desiccator, and weigh the precipitate to determine the recovery of barium carrier as barium chloride [$BaCl_2 \cdot 2H_2O$ - air-dried, $BaCl_2$ - oven-dried].
14. Count the beta activity of the precipitate to determine the barium 140 using a low-background beta counter. RECORD THE TIME AND DATE OF COUNTING (T_2).
15. Add enough 6N NH_4OH to the supernate from Step 8 to adjust the pH to 7 as indicated by universal pH paper. Add sufficient 3N Na_2CO_3 (∿5 ml) to the supernate to precipitate strontium carbonate. Centrifuge, and when completeness of precipitation has been verified by adding a few drops of Na_2CO_3, decant the supernate. Wash the strontium carbonate precipitate with 0.1N Na_2CO_3. Centrifuge again, and decant the supernate.
16. Dissolve the carbonate precipitate in 5 ml 6N HNO_3. Cautiously add 20 ml fuming HNO_3 to the solution, and cool in an ice bath for 10 minutes. Centrifuge, and decant the acid supernate.
17. Dissolve the strontium nitrate precipitate in 10 ml distilled water, and add 30 ml fuming HNO_3. Cool in an ice bath, centrifuge, and decant the acid supernate. RECORD THE TIME OF DECANTATION AS THE BEGINNING OF YTTRIUM 90 INGROWTH (T_3). Drain excess acid from the precipitate by inverting the centrifuge tube on paper towels.
18. Store the strontium nitrate precipitate for 1 to 2 weeks to allow yttrium 90 to grow in.
19. After a suitable ingrowth period, pipet 1.0 ml yttrium carrier solution into the centrifuge tube. Then add 1.0 ml 8N HNO_3, and warm gently to dissolve the precipitate. Add 10 ml fuming HNO_3, and cool in an ice bath for 10 minutes. Centrifuge, and quantitatively decant the supernate into a 60-ml separatory funnel. RECORD THE TIME AND DATE OF DECANTATION AS THE END OF YTTRIUM 90 INGROWTH AND THE BEGINNING OF ITS DECAY IN THE YTTRIUM FRACTION, AND THE BEGINNING OF YTTRIUM 90

INGROWTH INTO THE STRONTIUM PRECIPITATE (T_4). Save the strontium nitrate precipitate for Step 31. Drain excess acid by inverting the centrifuge tube on paper towels.

20. Make the solution in the separatory funnel 14N in HNO_3 by adding 4 ml distilled water. Add 10 ml pre-equilibrated TBP to this solution.
21. Equilibrate by shaking the funnel for approximately 2 to 3 minutes. Allow enough time for the phases to separate completely, and then drain off the aqueous phase and discard it.
22. Add 15 ml of 14N HNO_3 to the separatory funnel, and shake again for 2 to 3 minutes. When the phases have separated completely, drain off the aqueous phase and discard it.
23. Repeat Step 22.
24. Add 15 ml distilled water to the funnel and equilibrate for 2 to 3 minutes to extract yttrium from the organic phase. Let the phases separate completely. Then drain the aqueous phase into a 40-ml centrifuge tube.
25. Repeat Step 24, using 15 ml of 0.1N HNO_3 instead of distilled water. Drain the aqueous phase into the same 40-ml centrifuge tube used in Step 24.
26. To precipitate yttrium oxalate, add 5 ml 2N oxalic acid, and adjust the solution to pH 1.5 with 15N NH_4OH ($\sim$2 ml), using a pH meter. Stir, and cool in an ice bath for about 20 minutes. Centrifuge, discard the supernate, and save the oxalate precipitate for Step 28.
27. Weigh a stainless steel planchet and a 2.5-cm diameter membrane filter. Place the membrane filter into the suction-filtration apparatus.
28. Wash the oxalate precipitate with 10 ml distilled water, and transfer it to the filter. Using 10 ml of cold distilled water, wash both the precipitate and the centrifuge tube. Dry the precipitate with three 20-ml portions of absolute ethyl alcohol and three 10-ml portions of diethyl ether. Continue the suction for 2 minutes.
29. Transfer the membrane filter with the precipitate to the tared planchet. After the precipitate has reached room temperature in 10 to 15 minutes, weigh it and the filter. Calculate the recovery of yttrium carrier as yttrium oxalate [$Y_2(C_2O_4)_3$].
30. Count the beta activity of yttrium 90 in the precipitate in a low background beta counter. RECORD THE TIME OF COUNTING (T_5). Be sure

the filter is centered on the planchet to insure constant geometry during counting. Count again after 3 days to check that yttrium 90 is not contaminated by other radionuclides.

31. Dissolve the strontium nitrate precipitate obtained in Step 19 in 10 ml distilled water, and add 3 ml 15N NH_4OH. Heat to near boiling in a hot water bath, and add 10 ml 1N ammonium oxalate to precipitate the strontium oxalate. Cool in an ice bath, centrifuge, and decant the supernate.
32. Weigh a stainless steel planchet and a 2.5-cm diameter membrane filter. Place the filter in the filtration apparatus.
33. Use three 10-ml portions of cold distilled water to transfer the strontium oxalate precipitate to the filter. Wash the precipitate with three 10-ml portions of absolute ethyl alcohol and dry it with three 10-ml portions of diethyl ether. Continue suction for 2 minutes.
34. Transfer the filter and precipitate to the tared planchet, and reweigh after a delay of 10 to 15 minutes. Calculate the recovery of strontium carrier.

    [Note: After the precipitate has been counted, strontium carrier recovery may also be determined by flame photometry by dissolving the oxalate precipitate in distilled water and following the stepwise procedure given in 4.3.1.]
35. Count the precipitate in a low-background beta counter to determine the beta activity of total radiostrontium. RECORD THE TIME AND DATE OF COUNTING (T_6).

Calculations

$$\text{strontium 90 activity (pCi/gram of ash)} = \frac{A}{B \times C \times D \times E \times F \times G}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of yttrium carrier [Step 29]

C = recovery of strontium carrier [Step 34]

D = efficiency for counting yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

E = weight of ash (grams)

F = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from separation of yttrium in Step 19 [T_4] to the time of counting in Step 30 [T_5]

G = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from the beginning of the period in Step 16 [T_3] to the separation of yttrium from strontium in Step 19 [T_4]

$$\text{strontium 89 activity (pCi/gram of ash)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G \times H + I \times J)\right]$$

where A = net beta count rate of total radiostrontium (cpm)

B = efficiency for counting strontium 89 as strontium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting in Step 25 [T_3]

D = recovery of strontium carrier [Step 26]

E = weight of ash (grams)

F = strontium 90 activity (pCi/gram of ash)

G = self-absorption correction factor for strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter

H = efficiency for counting strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

I = efficiency for counting yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from the beginning of the period in Step 16 [T_3] to the separation of yttrium from strontium in Step 19 [T_4]

$$\text{barium 140 activity (pCi/gram of ash)} = \frac{A}{[B \times C \times D][E + (1.15 \times F \times G)]}$$

where A = net beta count rate of barium 140 (cpm)

B = recovery of barium carrier [Step 13]

C = weight of ash (grams)

D = correction factor $e^{-\lambda t}$ for barium 140 decay, where t is the time from sample collection to the time of counting in Step 14 $[T_2]$

E = efficiency for counting barium 140 as barium chloride mounted on a 2.4-cm diameter filter (cpm/pCi)

F = efficiency for counting lanthanum 140 as lanthanum chloride mounted on a 2.4-cm diameter filter (cpm/pCi)

G = correction factor $1-e^{-0.015t}$ for the ratio of lanthanum 140 to barium 140 activity, where t is the time from the barium separation in Step 10 $[T_1]$ to the time of counting $[T_2]$

1.15 = the ratio of lanthanum 140 activity to barium 140 activity when the mixture is in transient equilibrium. This factor is obtained by reducing the "ingrowth equation" for transient equilibrium when barium 140 is corrected for decay from the time of lanthanum separation.

Reference

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

4.2.4 Radium 226

The National Center for Radiological Health analyzes radium 226 in samples of food by the RADON 222 EMANATION METHOD. Radium 226 in bone, vegetation, or any sample which has been reduced to an ash can be analyzed by the same procedure, which is very similar to that used for analysis of radium 226 in water (see 5.2.4 of SECTION 5). The method allows a high degree of precision, and is specific for radium 226 as long as the alpha activity of the scintillation cell is not counted until the thoron (^{220}Rn) and actinon (^{219}Rn) daughters of any radium 224 and radium 223 present have had time to decay out.

Extensive laboratory facilities and experienced technicians are required to perform the analysis successfully. The procedure is completed in approximately 30 days; however, continuous processing will enable analysis of a large number of samples. The number which can be analyzed in a month is limited by the amount of equipment available.

Two very similar procedures are used by the Center's laboratories in analyzing samples by the radon emanation method. PROCEDURE A differs from PROCEDURE B in the number of precipitation steps and in the volume of the radon bubbler.

RADON 222 EMANATION METHOD — PROCEDURE A

Principle of Method

A weighed portion of an ashed sample is dissolved with nitric acid and hydrogen peroxide. Barium carrier is added, and carbonates are precipitated from the solution by adding ammonium carbonate. The carbonate precipitate is dissolved in nitric acid, and the solution is buffered. Ammonium dichromate reagent is added while the pH of the mixture is carefully controlled at 6.5 to precipitate radium-barium chromate.

The chromates are dissolved in hydrochloric acid. Barium chloride is then precipitated with hydrochloric acid-diethyl ether reagent. The radium-barium chloride precipitate is dissolved in water, and the solution is transferred to an emanation tube (radon bubbler) and stored for at least 28 days to allow the radium 226 to reach secular equilibrium with its daughters.

After secular equilibrium has been attained, the radon 222 is removed to a scintillation cell by de-emanating the bubbler. The cell is stored for at least four hours until the radon 219 and radon 220 daughters, if present, have decayed out and radon 222 has come into equilibrium with its daughters. At equilibrium, three alpha particles will be counted for each radon 222 disintegration. After a suitable storage period, the alpha activity of the scintillation cell is counted in a radon counter.

Reagents

acetic acid, CH_3COOH: 6N

ammonium acetate, $NH_4C_2H_3O_2$: 6N

ammonium carbonate, $(NH_4)_2CO_3$: saturated solution, 5% w/v

ammonium dichromate, $(NH_4)_2Cr_2O_7$: 0.5N (pH 6.5), 0.05N (pH 6.5)

ammonium hydroxide, NH_4OH: concentrated (15N), 6N

Ascarite: 20-30 mesh

carrier solutions:

Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 10 mg Ba^{+2} per ml, 1 mg Ba^{+2} per ml

hydrochloric acid, HCl: concentrated (12N), 5% v/v in absolute alcohol

hydrochloric acid-diethyl ether, $HCl—(C_2H_5)_2O$: 1:1 v/v solution

hydrogen peroxide, H_2O_2: 30% solution

magnesium perchlorate, $Mg(ClO_4)_2$: anhydrous (10-20 mesh)

nitric acid, HNO_3: concentrated (16N), 3N

Apparatus

analytical balance

drying tube, 5-mm diameter by 10 cm long

emanation apparatus: radon bubbler, manometer, and associated tubing as shown in Figures 4.2.4-1 and 4.2.4-2

filter stick, medium-porosity

needle valve

scintillation cell: See Figure 4.2.4-3. The cells used in PROCEDURE A have a 1/8-inch thick quartz glass window, the inner surface of which is coated with tin oxide. The collar above the Kovar metal chamber is of copper rather than brass.

silicone grease

suction-filtration apparatus: Millipore Pyrex Hydrosol Microanalysis filter holder, or equivalent

radon counter

Procedure

1. On an analytical balance, weigh 5 grams of ashed sample into a 400-ml beaker.
2. Add enough 16N HNO_3 and 30% H_2O_2 to dissolve the sample by heating and evaporating the solution to near dryness on a hot plate. Repeat this process, adding HNO_3 and H_2O_2 as necessary, until the ash is completely dissolved. Do not allow the sample to evaporate to dryness.
3. Add distilled water to bring the volume of solution to at least 150 ml. Heat it on a hot plate and add a few milliliters of 16N HNO_3 to insure complete solution. Disregard any flocculent precipitate of phosphate that may be present.
4. Add 5 mg barium carrier and make the solution alkaline (pH >7) with NH_4OH. Add 30 ml saturated ammonium carbonate solution, and allow the resulting precipitate to settle for 30 minutes.
5. Collect the precipitate by filtration through a medium-porosity filter stick, or by centrifugation. Discard the filtrate or supernate. Using hot 5% ammonium carbonate solution, wash the precipitate several times, and discard the wash.
6. Dissolve the carbonate precipitate with 3N HNO_3. Using a minimum volume of 3N HNO_3, wash the walls of the beaker and the filter stick or centrifuge bottle, and add the wash to the solution.
7. Add 100 mg barium carrier to the mixture, and bring the total volume of sample to 150 ml with 3N HNO_3. Heat on a hot plate until the precipitate is completely dissolved.
8. With 6N NH_4OH or 3N HNO_3, adjust the solution to pH 4.2-4.6. Add 3 ml 6N acetic acid and 10 ml 6N ammonium acetate. While stirring, slowly add 10 ml 0.5N ammonium dichromate solution at pH 6.5. Carefully control the pH at 6.5.
9. Allow the chromate precipitate to settle for 30 minutes. Collect

the precipitate by filtration through a filter stick or by centrifugation. Discard the filtrate or supernate. Wash the precipitate with 0.05N ammonium dichromate solution at pH 6.5, and discard the wash. Be sure to maintain a pH of 6.5 throughout the washing operation.

10. Dissolve the precipitate in 12N HCl. Wash the beaker walls and the filter stick (or centrifuge tube) with 12N HCl, and add the wash solution to the dissolved precipitate. Heat on a hot plate, and if necessary, add more HCl to completely dissolve the precipitate.
11. Remove the sample from the hot plate and chill it in an ice bath. In a hood, add 30 ml HCl-diethyl ether reagent. Cool the sample in an ice bath for 20 minutes. Then collect the precipitate by filtration through a medium-porosity filter stick that has been washed with the HCl-diethyl ether reagent. Discard the filtrate. Wash the barium-radium chloride precipitate [$Ba(Ra)Cl_2$] with 5% HCl in absolute alcohol, and discard the wash.
12. Dissolve the barium-radium chloride precipitate in no more than 8 ml distilled water. Use no more than 4 ml distilled water to transfer the sample to an emanation tube and to wash the beaker and funnel. The total volume in the emanation tube must be between 10 and 12 ml. Seal the tube, RECORD THE DATE AND TIME, and allow at least 28 days for the system to reach secular equilibrium. After this period, prepare and use the emanation apparatus as described in the following steps.
13. Attach a scintillation cell to a U-tube manometer as shown in Figure 4.2.4-1.

    [Note: Glass joints with O-ring seals are sometimes preferred because they require less stopcock grease than other types.]
14. Fill the drying tube half full of Ascarite; then fill to the top with anhydrous magnesium perchlorate. Attach the drying tube to the emanation tube (radon bubbler) containing the sample solution with a short piece of tubing. With another piece of tubing, attach the drying tube to a short length of thermometer capillary tubing, and attach the thermometer tubing to the manometer.
15. Open Stopcock 1, and apply a vacuum to the system.
16. When the mercury in the right-hand leg of the manometer reaches its maximum height, close Stopcock 1.

17. Leave the system in this configuration for 3 to 5 minutes to test for leaks. If the mercury begins to drop, check the glass joints and tubing connections for leaks. If necessary, apply a very light coating of silicone grease to the leaking connections. Then repeat Steps 16 and 17.
18. Open Stopcocks 1 and 2 and allow the mercury in the right-hand leg of the manometer (as shown in Figure 4.2.4-1) to reach its maximum height. Close Stopcock 1 and check for leaks as in Step 17.
19. With tubing, connect a tank of dry, aged air to the radon bubbler. Limit the air pressure to 1-2 pounds. A needle valve should be placed between the air tank regulator and the bubbler to regulate the pressure unless the air tank has a 2-stage pressure regulator.
20. Open Stopcock 3 slowly to prevent a pressure surge. Open Stopcock 4 very slowly.
21. Regulate the air flow through the bubbler at a fairly constant rate by occasionally adjusting the pressure with Stopcock 4.
22. With Stopcock 4, control the flow of aged air through the bubbler so that the transfer of radon is completed within 25 to 30 minutes.
23. When the level of mercury in both legs of the manometer is the same (at atmospheric pressure), close Stopcocks 4, 3, and 2 in that order. RECORD THE DATE AND TIME.
24. Remove the scintillation cell and store it in a light-tight cabinet for 6 hours to allow radon daughters to grow in and any actinon or thoron to decay out.
25. Remove the purged bubbler. The emanation system is ready for the next sample.
26. Count the alpha activity of the scintillation cell in a radon counter.

Calculation

$$\text{radium 226 activity (pCi/gram of ash)} = \frac{A \times B}{C \times D \times E \times F}$$

where A = net alpha count rate of radon 222 and daughters in counts per hour (cph)

B = multiplicative correction factor $(e^{-\lambda t_1}/1-e^{-\lambda t_1})$ for radon 222 decay during the counting period, where t_1 is the duration of the counting period in hours and λ is the radon 222 decay constant

C = efficiency of the scintillation cell and counter for radon 222 detection obtained experimentally for each cell-counter system (cph ^{222}Rn/pCi ^{226}Ra)

D = correction factor $1-e^{-\lambda t_2}$ for radon 222 buildup in the radon bubbler, where t_2 is the time from the beginning of the storage period to the final de-emanation [Step 23], and λ is the decay constant for radon 222

E = correction factor $e^{-\lambda t_3}$ for radon 222 decay from the final de-emanation [Step 23] to the beginning of the counting period [Step 26], where t_3 is the time in hours from final de-emanation to the beginning of the count, and λ is the radon 222 decay constant

F = weight of ash analyzed (grams)

Note that the decay constants must be expressed in reciprocal hours in this formula, and that the count rate is the average count rate over the entire counting period expressed in counts per hour.

The efficiency term C takes into account the 3 to 1 ratio of alpha counts per radon 222 disintegration. This efficiency or calibration factor must be determined experimentally for each cell counted on each radon counter to be used. A value of about 0.8 can be expected.

Efficiency of de-emanation need not be determined as long as the bubbler is de-emanated over at least a 20-minute period. Under these conditions, the efficiency of de-emanation is 100 percent.

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Rushing, D. E. *Radium-226 in Water (Total, Suspended, and Dissolved) by Radon De-emanation.* U. S. Department of Health, Education, and Welfare, Public Health Service, Division of Water Supply and Pollution Control, Colorado River Basin Water Quality Control Project Laboratory, Salt Lake City

Shearer, S. D., Jr. *The Leachability of Radium 226 from Uranium Mill Waste Solids and River Sediments.* Ph. D. dissertation, Department of Civil Engineering, No. 603, University of Wisconsin, Madison (1962) 162 pp [Available through Dissertation Abstracts, University of Michigan, Ann Arbor]

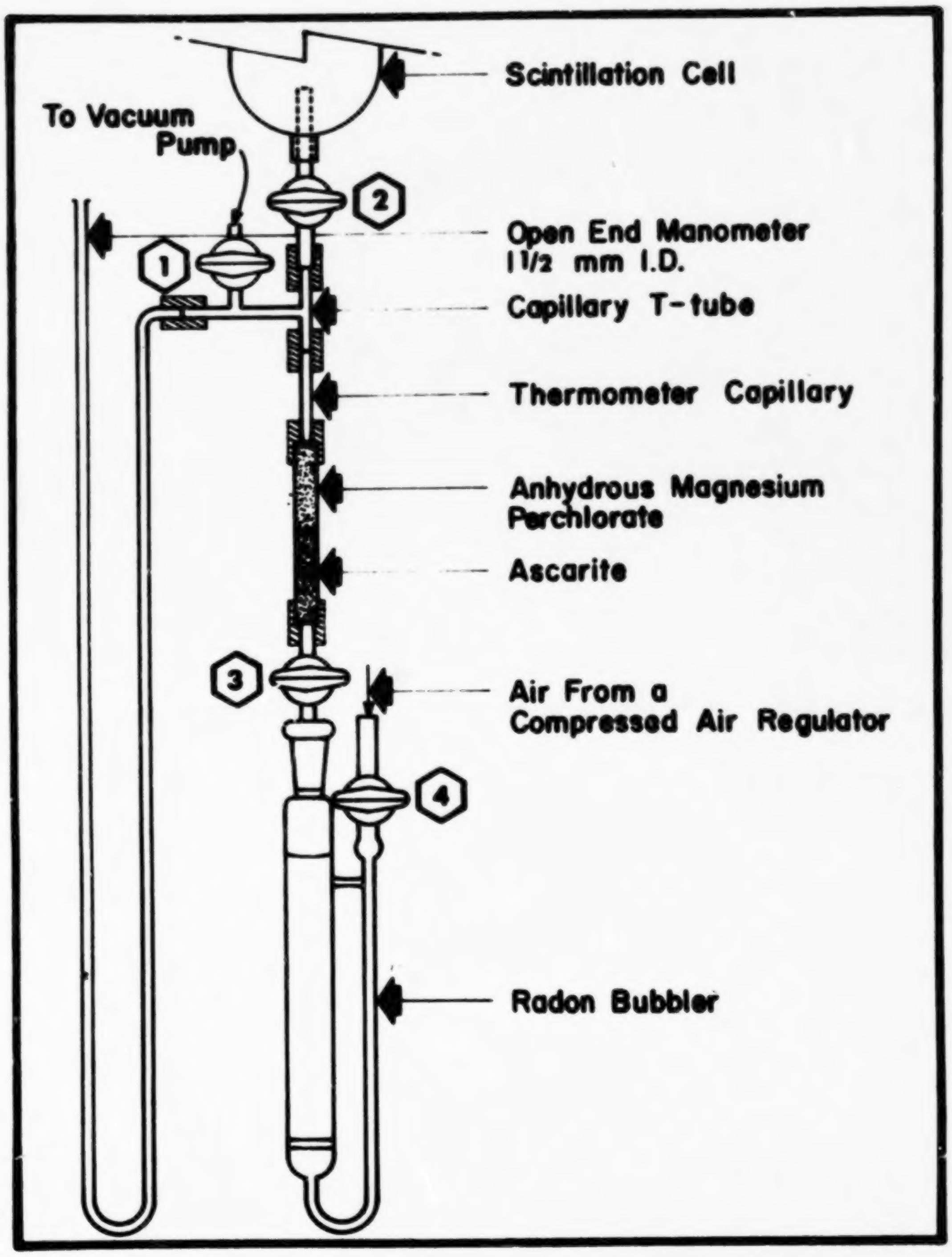
Scintillation Cell
To Vacuum Pump
Open End Manometer 1 1/2 mm I.D.
Capillary T-tube
Thermometer Capillary
Anhydrous Magnesium Perchlorate
Ascarite
Air From a Compressed Air Regulator
Radon Bubbler
1
2
3
4

Figure 4.2.4-1 The radon emanation apparatus for PROCEDURE A

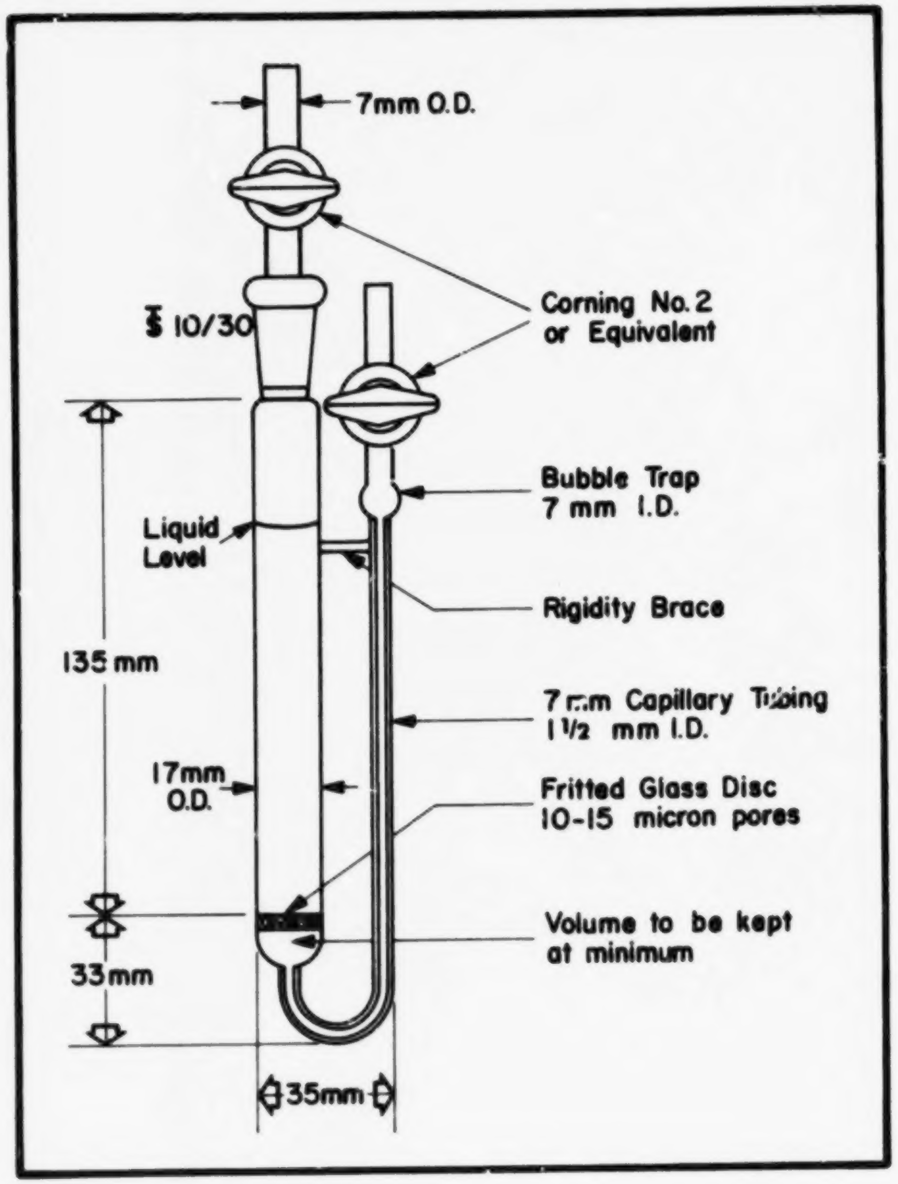
7mm O.D.
Corning No. 2
or Equivalent
$ 10/30
Bubble Trap
7 mm I.D.
Liquid
Level
Rigidity Brace
135 mm
7 mm Capillary Tubing
1½ mm I.D.
17mm
O.D.
Fritted Glass Disc
10-15 micron pores
Volume to be kept
at minimum
33mm
35mm

Figure 4.2.4-2 A radon bubbler (emanation tube)

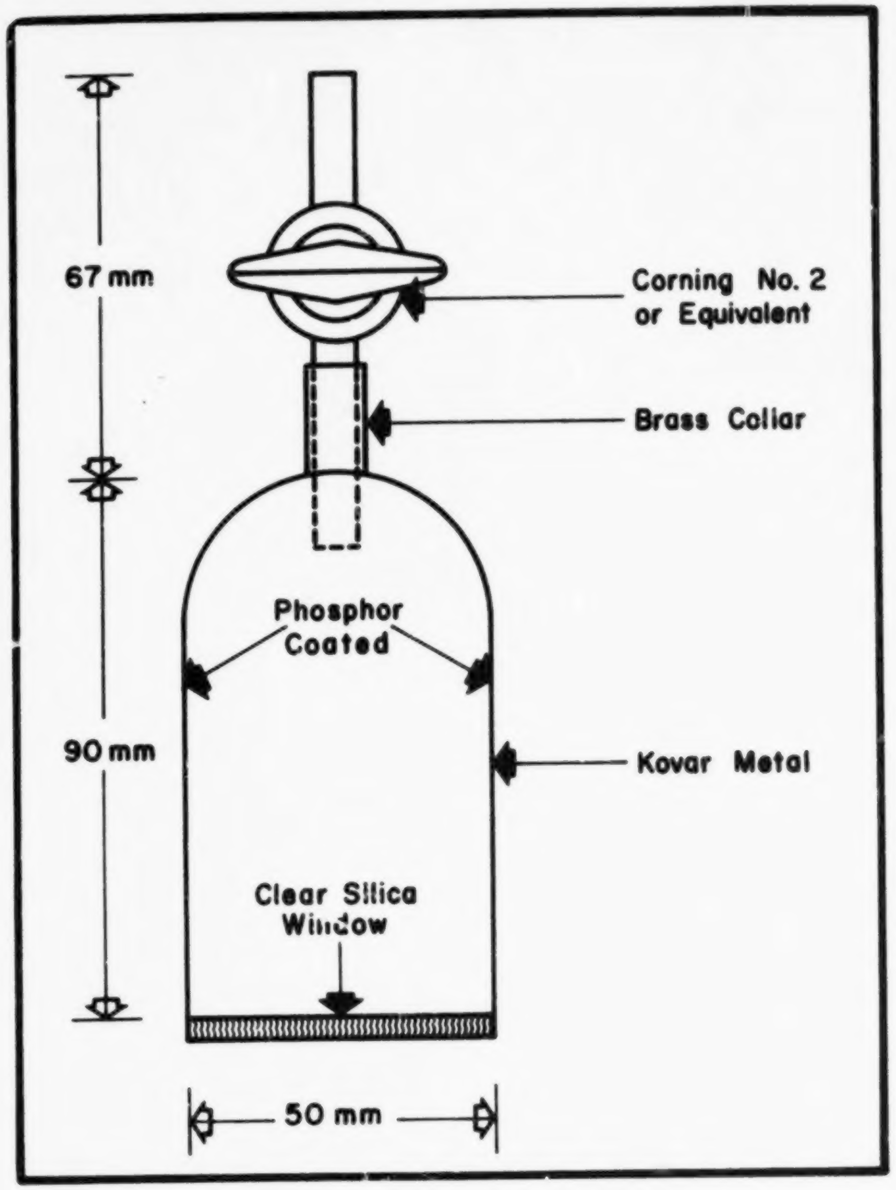
67 mm
Corning No. 2
or Equivalent
Brass Collar
Phosphor
Coated
90 mm
Kovar Metal
Clear Silica
Window
50 mm

Figure 4.2.4-3 A typical scintillation cell for radon counting

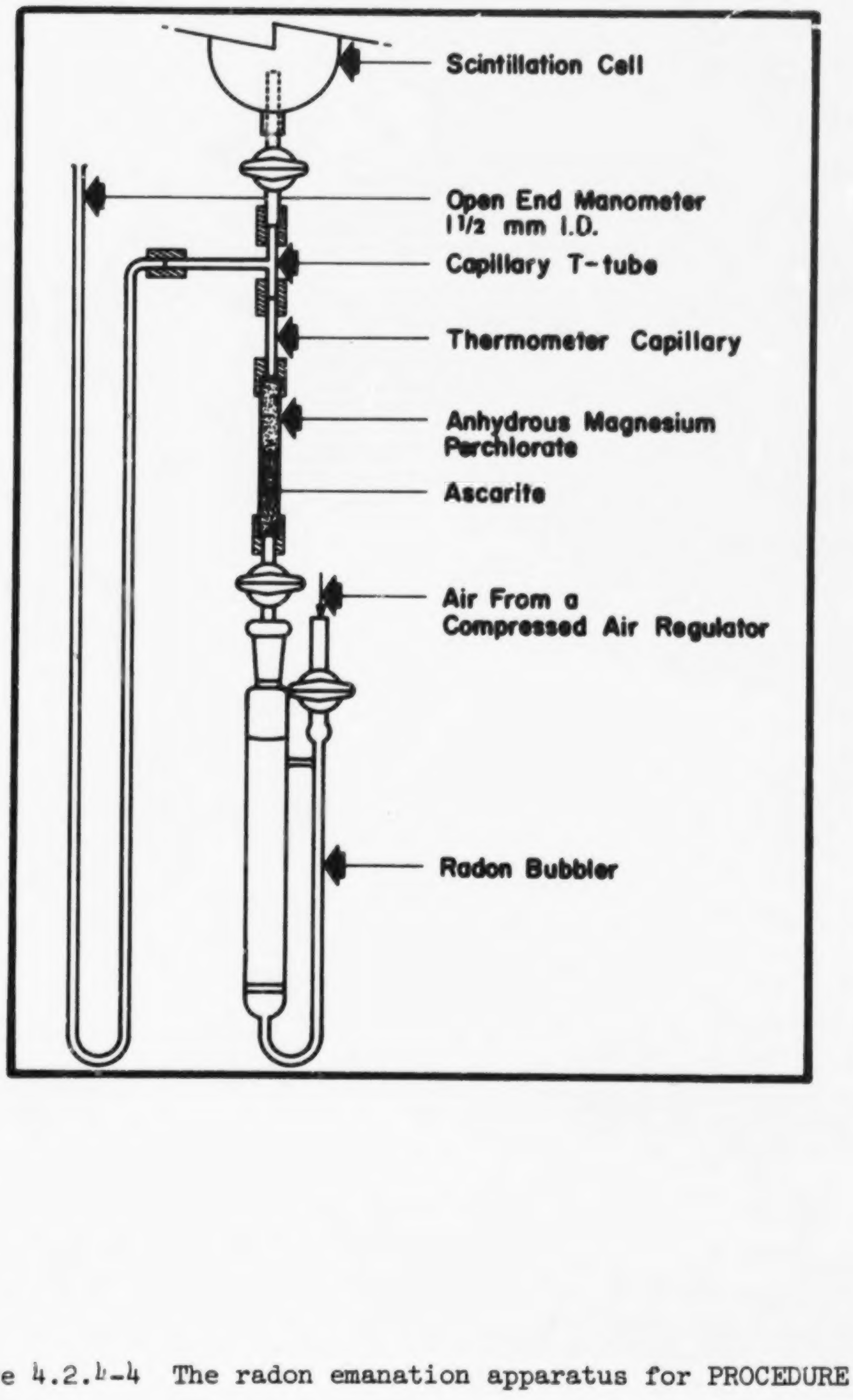
Scintillation Cell
Open End Manometer 1½ mm I.D.
Capillary T-tube
Thermometer Capillary
Anhydrous Magnesium Perchlorate
Ascarite
Air From a Compressed Air Regulator
Radon Bubbler

Figure 4.2.4-4 The radon emanation apparatus for PROCEDURE B

RADON 222 EMANATION METHOD – PROCEDURE B

Principle of Method

A sample of ashed food is dissolved in nitric acid. Barium carrier and barium 133 tracer are added to the solution, and the radium is co-precipitated with barium sulfate. The sulfate precipitate is converted to the carbonate which is then dissolved in nitric acid. Barium carrier recovery is determined by counting the gamma activity of barium 133 tracer in this solution.

The solution is de-emanated and then aged for at least 2 weeks to allow radon 222 to grow in. After a sufficient storage period, the solution is again de-emanated, and the radon is collected in a scintillation cell. The alpha activity in the scintillation cell is measured in a radon counter.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N), 6N
ammonium sulfate, $(NH_4)_2SO_4$: 50% w/v
Ascarite: 20-30 mesh
barium 133 tracer solution: ∿0.02 μCi ^{133}Ba per ml
carrier solution:
  Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
hydrochloric acid, HCl: concentrated (12N)
magnesium perchlorate, $Mg(ClO_4)_2$: anhydrous (10-20 mesh)
nitric acid, HNO_3: concentrated (16N)
sodium carbonate, Na_2CO_3: 3N

Apparatus

analytical balance
compressed air, aged
drying tube, 100 mm long by 8 mm in diameter
emanation apparatus: radon bubbler (Figure 4.2.4-2), scintillation cell (Figure 4.2.4-3), and other associated apparatus as shown in Figure 4.2.4-4.
gamma scintillation counter
magnetic stirrer with stirring bars

plastic container, flat-bottomed, used as a sample container for counting gamma activity of a solution

radon counter

vacuum pump

Procedure

1. Dissolve a weighed portion of food ash in a 400-ml beaker. Add 1.0 ml of barium 133 tracer solution and 1.0 ml of barium carrier solution, and dilute to 250 ml with distilled water.
2. While stirring, add 50 ml 16N HNO_3 and 5 ml 50% ammonium sulfate. Mix for 30 minutes, using a magnetic stirrer.
3. Allow the sulfate precipitate to settle, and aspirate most of the supernate to waste. Transfer the precipitate to a 40-ml centrifuge tube with distilled water. Centrifuge, and discard the supernate.
4. Add 30 ml 3N Na_2CO_3 to the precipitate and heat in a boiling water bath for 30-60 minutes, stirring frequently. Cool the sample, centrifuge it, and discard the supernate.
5. Dissolve the precipitate in a minimum volume (~2 ml) 16N HNO_3, and with distilled water transfer the solution to a plastic sample container.

   [Note: If the precipitate does not dissolve completely, centrifuge the sample, decant the supernate into the plastic container, and repeat Steps 4 and 5 on the residue until the sample is completely dissolved.]
6. Dilute the solution in the plastic container to 25 ml with distilled water. Measure the activity of barium 133 in a gamma scintillation counter and calculate the recovery of barium carrier by dividing the measured activity by the activity of 1.0 ml of tracer solution in a 25-ml volume.
7. Transfer the solution to a radon bubbler (emanation tube). Attach a vacuum pump to the upper stopcock of the bubbler. Open the lower stopcock and then slowly open the upper stopcock. Purge the system of radon by slowly drawing air through the bubbler for about 20 minutes.
8. Close the lower stopcock and evacuate the bubbler for about 3 minutes. Close the upper stopcock. RECORD THE TIME AND DATE AS THE BEGINNING OF RADON 222 INGROWTH (T_1). Store the solution in the emanation tube for at least 2 weeks.

9. Fill the lower half of a drying tube with Ascarite and the upper half with anhydrous magnesium perchlorate. Assemble the emanation apparatus as shown in Figure 4.2.4-4, and attach the radon bubbler and a previously evacuated scintillation cell.
10. Open the stopcock on the scintillation cell, then the upper stopcock of the bubbler. Slowly open the lower stopcock of the bubbler. Allow the air to pass through the solution into the scintillation cell until the system reaches atmospheric pressure as indicated by the manometer. Close the stopcock of the scintillation cell. RECORD THE TIME AND DATE AS THE BEGINNING OF THE DECAY OF RADON 222 (THE END OF RADON 222 INGROWTH) AND THE BEGINNING OF THE INGROWTH OF RADON 222 DAUGHTERS (T_2).
11. Store the scintillation cell for at least 2 hours to allow radon 222 daughters to grow in. Count the alpha activity of the scintillation cell in a radon counter. RECORD THE DATE AND TIME OF COUNTING (T_3) to determine the correction for ingrowth of radon 222 daughters.

Calculation

$$\text{radium 226 activity (pCi/gram of ash)} = \frac{A}{B \times C \times D \times E \times F}$$

where A = net alpha count rate of the scintillation cell in counts per hour (cph)

B = efficiency of the scintillation cell and counter for detecting radon 222, obtained experimentally for each cell-counter system (cph ^{222}Rn/pCi ^{226}Ra)

C = barium carrier recovery as measured with barium 133 tracer in Step 6

D = correction factor $1-e^{-\lambda t}$ for radon 222 ingrowth, where t is the time in hours from T_1 [Step 8] to T_2 [Step 10], and λ is the radon 222 decay constant

E = correction factor $1-e^{-\lambda t}$ for radon 222 decay (radon daughter ingrowth) between final de-emanation and counting, where t is the time in hours from T_2 [Step 10] to T_3 [Step 11], and λ is the radon 222 decay constant

F = weight of ash analyzed (grams)

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Holaday, D. A., D. E. Rushing, R. D. Coleman, P. F. Woolrich, H. L. Kusnetz, and W. F. Bale. *Control of Radon and Daughters in Uranium Mines and Calculations on Biologic Effects*. U. S. Department of Health, Education, and Welfare, Public Health Service, Public Health Service Publication No. 494 (1957)

Magno, P. J., E. J. Baratta, and E. Ferri. *Procedures for the Chemical and Radiochemical Analysis of Environmental Samples*. Winchester, U. S. Department of Health, Education, and Welfare, Public Health Service, Northeastern Radiological Health Laboratory Report No. NERHL-64-1 (1964)

4.3 DETERMINATION OF STABLE ELEMENTS

4.3.1 Strontium Carrier

FLAME PHOTOMETRIC METHOD

The recovery of strontium carrier in any radiostrontium determination can be measured by flame photometry. The stepwise procedure for the analysis can be obtained from the operating manual provided with the spectrophotometer. Errors in the recovery determination are largely compensated by parallel flame analysis of the sample and a control sample.

Principle of Method

The strontium nitrate precipitate, produced during radioanalysis as one of the end products after the ingrowth and removal of yttrium 90, is dissolved in distilled water and diluted to volume. The strontium content of the sample is determined by flame photometry at a wavelength of 460 millimicrons using an oxyacetylene flame. The reading obtained from the sample is compared with a calibration curve prepared by recording the readings obtained from several dilutions of a strontium standard solution.

Reagents

strontium standard solutions:

Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: volumetrically diluted from the strontium carrier solution to 0.40, 0.02, 0.015, 0.010, and 0.005 mg Sr^{+2} per ml

Apparatus

atomizer burners

flame spectrophotometer: Beckman DU Spectrophotometer or equivalent equipped with flame attachment, blue phototube, and medium-bore oxyacetylene burner

oxyacetylene fuel

Procedure

1. Dissolve the strontium nitrate precipitate in the planchet in distilled water, and quantitatively transfer it to a 25-ml volumetric flask. Dilute to volume with distilled water.
2. Prepare a calibration curve by transferring a portion of each dilution of the strontium standard solution to a 5-ml beaker and atomizing it. Plot the concentrations of the standard solution dilutions along the abscissa of a linear-coordinate graph and plot the corresponding percent transmission values (recorder peak heights) along the ordinate.
3. Transfer a portion of the diluted sample solution to a 5-ml beaker. Atomize it, and record the response.
4. Dilute an aliquot of the strontium carrier solution used in the procedure by which the sample was analyzed for strontium to 25 ml in a volumetric flask. The aliquot diluted should be equal in volume to the aliquot of carrier solution added to the sample in the analytical procedure. Transfer a portion of the diluted carrier solution to a 5-ml beaker. Atomize it and record the response.
5. Read the concentration of strontium in the diluted sample and in the diluted carrier from the calibration curve. Correct each concentration value for the dilution, and calculate the carrier recovery.

Calculation

$$\text{strontium carrier recovery (decimal percentage)} = \frac{A}{B}$$

where A = concentration of strontium in the sample

B = concentration of strontium in the carrier solution

Note: This procedure is almost identical to that given in 1.3.1 of SECTION 1. MILK.

4.3.2 Calcium

PERMANGANATE TITRATION PROCEDURE

The permanganate titration procedure may be used to determine the calcium in any sample for which ashing is used for preliminary concentration. The analysis is not difficult to perform and no special apparatus is required. It is very similar to the procedure given in 3.3.2 of SECTION 3. MILK.

Principle of Method

Calcium oxalate is precipitated from a portion of an ashed food sample which has been dissolved in a weakly acid solution (pH 3.5 to 4.0). The precipitate is washed, dissolved in dilute sulfuric acid, and titrated with potassium permanganate.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N)
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N
potassium permanganate, $KMnO_4$: 0.05N standardized
sulfuric acid, H_2SO_4: 2N

Apparatus

burette

Procedure

1. Pipet a portion of a dissolved ashed sample estimated to contain between 25 and 50 mg of calcium into a 40-ml centrifuge tube. Dilute to 30 ml with distilled water.
   [Note: A blended dietary food sample contains approximately 0.5 to 1.0 gram of calcium per kilogram.]
2. Add 5 ml of 2N oxalic acid to the solution. Adjust the pH to 3.5-4.0 with 15N NH_4OH. Centrifuge, and discard the supernate.
3. Add 40 ml hot distilled water to the precipitate. Mix well. Centrifuge, and discard the supernate.
4. Repeat Step 3.

5. Dissolve the precipitate in 2N H_2SO_4. With distilled water, dilute the solution to 10 ml, and transfer it to a 125-ml Erlenmeyer flask. Heat on a hot plate to 90° C.
6. Titrate the hot solution with standardized 0.05N $KMnO_4$ to a faint pink color which persists for at least 30 seconds.

Calculation

$$\text{calcium concentration (grams Ca/gram of ash)} = \frac{A \times B \times C \times D}{E \times F}$$

where A = volume of $KMnO_4$ used for titration (ml)

B = normality of $KMnO_4$ [average of 3 standardizations] (meq/ml)

C = milliequivalent weight of calcium (mg/meq)

D = volume of diluted ash analyzed (ml)

E = total volume of dissolved ash (ml)

References

Hillebrand, W. F., G. E. F. Lundell, H. A. Bright, and J. I. Hoffman. *Applied Inorganic Analysis*. 2nd Ed., New York, Wiley (1953)

Furman, N. H., ed. *Standard Methods of Chemical Analysis, Vol. I.* 5th Ed., Princeton, Van Nostrand (1962)

4.3.3 Potassium

GAMMA SPECTROMETRY

Potassium in food samples is conveniently measured by gamma pulse height analysis of potassium 40, which occurs as a constant proportion (0.0119 percent) of natural potassium. A 3.5-liter portion of the food sample blended as described in 4.1.1 of 4.1 PREPARATION OF SAMPLES is placed in a Marinelli-type beaker which fits over a 4-inch by 4-inch thallium-activated sodium iodide crystal detector. Potassium 40 in the blended sample is measured, and the concentration of natural potassium is computed.

After being analyzed for potassium by this non-destructive method, the sample can be ashed and analyzed for other stable or radioactive constituents.

The gamma pulse height analysis technique is discussed in SECTION 1. under GAMMA SPECTROMETER in part 1.1.3 Gamma Activity.

SECTION 5.

WATER

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SECTION 5. WATER

5.0 INTRODUCTION

Water may be sampled from a wide variety of sources. Sample types can range from surface waters, often high in suspended matter (silt, clay, humus, plankton) with or without industrial and domestic wastes, to a potable water which has undergone simple or complex purification, or pure ground water from a well or spring.

Since many species of radionuclide are adsorbed on particulate matter or are accumulated by living organisms, representative sampling of water containing suspended matter is often difficult, and extreme caution should be taken to assure proper sampling. Furthermore, since non-equilibrium conditions often prevail, sample preparation must be rapid enough to prevent substantial change in the radionuclide distribution. This is particularly important where filtrate radioactivity is to simulate residual radioactivity following conventional water purification, while the suspended activity plus the filtrate activity is to provide information on the total radioactivity of the water. Obviously, if the amount of suspended matter is low and/or the water is from a potable supply, the differentiation of suspended and filtrate radioactivity is neither necessary nor desirable. For this type of sample and for ground water of high solids content, it is more important to pretreat the sample with acid or another chemical agent to assure uniform distribution in subsamples taken after storage.

Water polluted with industrial or domestic wastes is subject to rapid chemical and biological change depending on chemical composition and physical conditions. These should be considered in relation to the objectives of studies on radionuclide content.

The Public Health Service performs routine water surveillance in three networks. These are a) the National Water Quality Network, which samples surface waters from the main streams and tributaries of the United States, b) the Drinking Water Analysis Program, which tests 100 to 200 municipal water supplies, and c) the Radiation Surveillance Network, which collects and analyzes precipitation samples.

The levels of radioactivity in National Water Quality Network surface waters have been monitored by the Water Pollution Surveillance Systems. There are about 130 sampling points, and the radioactivity monitoring consists primarily of gross alpha and gross beta determinations on both suspended solids and dissolved solids fractions of one-liter samples taken weekly. Weekly samples from selected sampling points are composited for determination of strontium 90 in the total sample. The methods by which gross radioactivity is measured in these surface waters are described in the 12th edition of *Standard Methods for the Examination of Water and Wastewater*(1). For strontium 90 measurement, a modified yttrium oxalate precipitation and counting procedure is used(2).

The Drinking Water Analysis Program deals with the water quality of Interstate Carrier water supplies and, therefore, with the application of the Public Health Service Drinking Water Standards(3). The Standards state that the examinations shall be performed according to the methods prescribed by the American Public Health Association, American Water Works Association, and the Water Pollution Control(1).

These water supplies are sampled by state and municipal public health personnel under the direction of the Interstate Carrier Branch of the Division of Environmental Engineering and Food Protection. Each sample is a composite of three subsamples collected each day for two weeks(4). Laboratories of the National Center for Radiological Health examine the samples for radioactivity. Examinations for gross alpha and gross beta-gamma activity are performed first, and samples showing alpha activity greater than 3 picocuries per liter or beta-gamma activity greater than 10 picocuries per liter are then scheduled for analysis of radium 226 or strontium 90 unless experience indicates no need for these analyses.

Precipitation from individual storms is collected at the Radiation Surveillance Network air sampling stations. Subsamples of water are evaporated to dryness and monitored for beta-gamma activity with a portable survey meter. The liquid subsamples or the concentrated sample solids are shipped to the Radiological Health Laboratory at the National Center for Radiological Health in Rockville, Maryland for measurement of gross beta-gamma activity, the beta gamma decay rate (if desired), and for measurement of gamma emitting radionuclides in samples exceeding a prescribed gross beta-gamma activity.

References

1. APHA-AWWA-WPCF. *Standard Methods for Examination of Water and Wastewater,* 12th Ed. New York, American Public Health Association, Inc. (1965)

2. Division of Water Supply and Pollution Control, Public Health Service. *Radiological Health Data and Reports, Vol. 6, No. 10.* U. S. Department of Health, Education, and Welfare, Division of Radiological Health (1965) p. 556

3. *Public Health Service Drinking Water Standards - 1962.* Public Health Service Publication No. 956, Washington, U. S. Government Printing Office (1962)

4. Division of Environmental Engineering and Food Protection and Division of Radiological Health, PHS, "Drinking water analysis program 1962". *Radiological Health Data and Reports, Vol. 6, No. 10.* U. S. Department of Health, Education, and Welfare, Public Health Service, Division of Radiological Health (1965) p. 559

5.1 PREPARATION OF SAMPLES

Glass or polyethylene bottles are appropriate vessels for the collection of samples. The examination of suspended and filtrate activities precludes the addition of carriers or preservatives such as acids, and includes the warning that there should be no undue delay in processing the sample after collection. Changes in the distribution of activity between water, solid particles, and container surface, and the physical decay of short-lived nuclides may or will occur during storage. When there is little or no suspended matter, the addition of appropriate carriers and preservative may be advisable.

Sample preparation is normally an integral part of the analytical procedure except for gamma spectrometry. This examination is usually non-destructive, *i.e.,* a 3.5-liter sample of clear water is poured into a Marinelli type beaker and counted. After counting, the sample is available for other tests. On the other hand, if suspended solids in the sample settle readily, a stabilizing agent such as a sequestering chemical agar-agar should be added to prevent fractionation during counting. Generally, gamma spectrometry can be improved for non-volatile radionuclides by first evaporating a relatively large sample to a small volume or to dry solids, thereby achieving better counting geometry and improved gamma resolution.

Clear water such as drinking water and impounded water requires no sample preparation. However, if prolonged storage will occur before analysis of radiostrontium, the sample should be pretreated with strontium carrier equal to that prescribed in the respective method and should be preserved by acidification to a pH of about 4.0.

Turbid waters on which a measurement of the total radiostrontium elements is desired require more stringent treatment. Addition of carrier and acidification to pH 4.0 should be followed by filtration and ignition and dissolution of filter and suspended matter, by digestion of residue in nitric acid, or, for stubborn residues, by carbonate fusion and acid digestion. The solubilized suspended matter is then returned to the original subsample for processing with account taken of the increase in sample volume.

For industrial waste effluents containing substantial quantities of suspended organic matter and an abundant concentration of radiostrontium, two courses of action may be taken to obtain a clear solution for the measurement of total strontium nuclides.

One is the wet combustion technique in which up to several hundred milliliters of sample are acidified with nitric acid, evaporated to a volume of 20 to 30 milliliters and transferred into 50- or 100-milliliter beakers or Erlenmeyer flasks. The sample is digested on a hot plate or in a water bath with equal volumes of water and concentrated nitric acid until only traces of organic matter remain. The residues are then treated with hydrogen peroxide in nitric acid solution or, in stubborn cases, with perchloric acid. Finally, the insoluble silica is removed by filtration and the filtrate is analyzed.

The other course of action is the evaporation of the entire sample in a Vycor or platinum evaporating dish, ignition in a muffle furnace, nitric acid digestion or carbonate fusion, nitric acid dissolution, and filtration to remove silica.

Although it is preferable to start with a clear solution, a moderate amount of pretreatment plus filtration is not likely to remove any of the radiostrontium elements.

On the other hand, if it is desired to measure the strontium nuclides in the suspended and filtrate fractions, the suspended matter should be separated and combusted by either the wet or dry techniques mentioned above.

5.2 DETERMINATION OF RADIONUCLIDES

Water may contain a large variety of different radionuclides. These may be either naturally occurring radionuclides such as thorium, uranium, or radium and its daughter products, or man-made isotopes from weapons test fallout, accelerators, reactors, or the medical and industrial applications of isotopes.

A knowledge of the radionuclide content of water is necessary to an evaluation of public health significance. Gross radioactivity in water may serve as an indicator for other sources of radiation exposure. Analytical methods for obtaining gross activities or specific radionuclide concentrations in water are included in this Section. These methods are currently used by the National Center for Radiological Health laboratories. Most of these procedures are suitable for examinations in an assembly line type of operation.

Detailed analytical procedures are described for gross alpha and gross beta-gamma activities in fresh water and for beta-gamma activity in saline water. Procedures are also given for analysis of total radiostrontium, strontium 90, total radium, radium 226, barium 140, and tritium in water as well as for select stable elements associated with these radionuclides. Analysis for gamma emitters is outlined and given by reference to the section on milk (SECTION 3). The methodology for counting radioactivity is similar to that given in other sections of this document. It should be noted that many procedures are designed for sequential examinations. For example, total radiostrontium may be determined as part of a strontium 90 determination.

The gross alpha determination is a screening method to indicate whether further radionuclide analysis is necessary. For waters low in suspended and dissolved matter, the measurement is reliable and informative for non-volatile emitters. However, alpha absorption by sample solids is excessive at sample solids thicknesses of 3 to 5 milligrams per square centimeter. This places a restriction on sample size when the solids in either the suspended or the filterable fractions are high. Even with long (60-minute) counting periods, the reliability of the assay of such samples is usually poor.

The gross beta-gamma measurement is also a screening method to indicate the general concentration of non-volatile beta-gamma emitters. Again, the assay is quite precise for waters of low solids content. However, when the sample solids thickness exceeds 15 to 20 milligrams per square centimeter, a variable loss of beta emission occurs, depending on the energy spectra of the nuclides contributing to the activity and the radionuclides used to calibrate the counter. For example, when a ^{90}Sr-^{90}Y standard is used for calibration, the high energy of the yttrium 90 emission will yield high efficiencies for counting relatively thick samples. When these factors are used to estimate other mixtures of beta emitters of relatively low energy, such as mixed fission products, the true beta activity will be grossly underestimated.

Measurement of gross activities in a moderate amount of suspended matter in brackish water can be fairly reliable, but a high salt content, as in sea water, prevents precise measurement of filtrate beta activity in more than about 10 milliliters of sample. Because there is interest in small amounts of activity in much larger samples of brackish water, techniques are used to separate most radionuclides of interest from the salt for a more precise screening test short of preforming a specific radiochemical examination.

5.2.1 Gross Alpha and Gross Beta Activity

GROSS ALPHA AND GROSS BETA ACTIVITY IN TOTAL RESIDUE

The radioactivity in water may consist of many different radionuclides either naturally occurring or man-made. The gross measurement provides a means of screening the samples to determine whether tests of radionuclides are necessary.

Gross alpha and beta activities are determined in the residue on evaporation of clear water such as the potable water supplies of interstate carriers. The latter are examined for compliance with the Public Health Service Drinking Water Standards(1)

Principle of Method

A sample of water is evaporated and the residue is transferred to a planchet for counting gross alpha and gross beta or beta-gamma activities.

Reagents

lucite: 0.5 mg/ml in acetone
nitric acid, HNO_3: 3N

Apparatus

internal proportional counter: capable of receiving and maintaining good electrical contact with counting pans; complete with preamplifier, scaler, timer, register, constant voltage supply, counting gas equipment, and counting gas (see SECTION 1).

planchets or counting pans: corrosion-resistant metal, about 50 mm in diameter, 6-10 mm in height, and thick enough to be serviceable for one-time use. [Stainless steel or aluminum pans are satisfactory, depending on the kind of sample and reagents added.]

Procedure

1. Measure into a beaker a volume of sample containing, for alpha, not more than 100 mg of residue and, for beta, not more than 200 mg of residue per 20 cm^2 of planchet, and evaporate to near dryness.
2. With distilled water, transfer the concentrate to a tared metal planchet.
3. Using a rubber policeman, wash beaker walls with a few drops of nitric acid.
4. Combine washings with water rinsings in the planchet, and evaporate to dryness.
5. Flame planchet to dull red; cool, and weigh. If the residue flakes, treat it with 5 to 10 drops of lucite solution and dry in an oven at 100° C to constant weight (∿10 minutes).

6. Store the sample in a desiccator until it is to be counted.
7. Count the gross alpha and the gross beta activity in an internal proportional counter (see SECTION 1).

Calculations

$$\text{gross alpha activity* (pCi/liter)} = \frac{A}{B \times C \times D}$$

where A = net alpha count rate (cpm)
B = efficiency for counting alpha activity in a "weightless" sample
C = volume of sample (liters)
D = correction factor for self-absorption in the sample

$$\text{gross beta activity** (pCi/liter)} = \frac{A}{B \times C \times D}$$

where A = net beta count rate (cpm)
B = efficiency for counting gross beta activity (cpm/pCi)
C = volume of sample (liters)
D = correction factor for self-absorption

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* If sample thickness exceeds 10 mg/cm^2, assume infinite thickness and report an approximate gross alpha assay, or repeat the test on a smaller portion of the sample.

** If the sample thickness exceeds 20 mg/cm^2, and ^{90}Sr-^{90}Y self-absorption factors are used, report beta-gamma activity rather than gross beta activity.

GROSS ALPHA AND GROSS BETA ACTIVITY IN DISSOLVED SOLIDS

Surface waters or waste effluents may contain radioactive elements associated specifically with the suspended matter as well as that which is dissolved or colloidal. It is usually important to measure the total radioactivity and also to separate the filtrate activity as that portion which is most likely to appear in the finished water following conventional water purification.

Principle of Method

Water samples containing suspended matter are filtered through an appropriate filter, and the filtrate is analyzed as a sample of clear or potable water. The filtered water sample is evaporated and the residue is transferred to a planchet for counting gross alpha and gross beta activity.

Reagents

lucite: 0.5 mg/ml in acetone
nitric acid, HNO_3: 3N

Apparatus

filters: membrane, such as Millipore Type HA; cellulose fiber, such as Whatman No. 41; or asbestos mat in a gooch crucible
filtration equipment: appropriate to the filter used
internal proportional counter: as described on page 5-8
planchets: corrosion-resistant metal, as described on page 5-8

Procedure

1. Filter a volume of sample containing not more than 100 mg of dissolved solids for alpha assay, or not more than 200 mg of dissolved solids for beta assay.
2. Add distilled water to wash the non-filterable solids on the filter. [Save the filter with suspended matter for separate analysis.]
3. Evaporate the filtrate to near dryness on a hot plate.
4. With distilled water, transfer the concentrate to a tared metal planchet.

5. Using a rubber policeman, wash the beaker walls with a few drops of nitric acid.
6. Combine washings with water rinsings in the planchet, and evaporate to dryness.
7. Flame the planchet to dull red; cool, and weigh. If the residue flakes, treat it with 5 to 10 drops of lucite solution and dry in an oven at 100° C to constant weight ($\sim$10 minutes).
8. Store the sample in a desiccator until it is to be counted.
9. Count the gross alpha and the gross beta activity in an internal proportional counter (see SECTION 1).

Calculations

$$\text{gross alpha activity* (pCi/liter)} = \frac{A}{B \times C \times D}$$

where A = net alpha count rate (cpm)
B = efficiency for counting alpha activity in a "weightless" sample (cpm/pCi)
C = volume of sample (liters)
D = correction factor for self-absorption in the sample

$$\text{gross beta activity** (pCi/liter)} = \frac{A}{B \times C \times D}$$

where A = net beta count rate (cpm)
B = efficiency for counting gross beta activity (cpm/pCi)
C = volume of sample (liters)
D = correction factor for self-absorption

Results are reported as gross alpha and gross beta activity in the dissolved solids per liter of sample.

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* If sample thickness exceeds 10 mg/cm^2, assume infinite thickness and report an approximate gross alpha assay, or repeat the test on a smaller portion of the sample.

** If the sample thickness exceeds 20 mg/cm^2, and ^{90}Sr-^{90}Y self-absorption factors are used, report beta-gamma activity rather than gross beta activity.

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GROSS ALPHA AND GROSS BETA ACTIVITY IN SUSPENDED SOLIDS

Surface water may contain invisible living organisms or suspended matter with which a substantial amount of non-volatile radioactivity may be associated. Industrial wastes in particular may have a large fraction of the total activity in the suspended matter. Since the fate of suspended and planktonic matter differs from that of dissolved matter, this fractional radioactivity may be important to measure as an environmental contaminant.

Principle of Method

Depending on the filterability of the water, an appropriate filtration system is used. For the purpose of approximately simulating conventional water filtration in purification plants, the sample is filtered through cellulose fiber or membrane filters. The filter containing the solids is transferred to a tared, metal planchet and is fixed and dried or ignited, depending on the filter used. The gross alpha and gross beta activities are measured in an internal proportional counter.

Reagents

acetone — diethyl ether, $(CH_3)_2CO - (C_2H_5)_2O$: 1:1 v/v solution
conducting fluid: Anstac AC
ethyl alcohol, C_2H_5OH: 95%
lucite: 0.5 mg/ml in acetone
nitric acid, HNO_3: 3N

Apparatus

filters: membrane, such as Millipore Type HA, or cellulose fiber, such as Whatman No. 41
filtration equipment: appropriate to the filter used
internal proportional counter: as described on page 5-8
planchets: corrosion-resistant metal, as described on page 5-8

Procedure

1. Filter a measured volume of sample, and wash the non-filterable solids on the filter with distilled water.
2. Process the filter containing the solids beginning with Step 3A, 3B,

or 3C, depending on the density thickness of the solids and the type of filter.

3A. When filtration is by membrane filter and the solids thickness is less than 5 mg/cm^2 for alpha counting or 10 mg/cm^2 for beta counting, place the filter in a tared planchet and air dry.

4A. Spread about 1 ml of acetone-ether reagent over the membrane to fix it to the planchet, and air dry.

5A. Moisten the solids with conducting fluid; then oven dry.

6A. Desiccate to constant weight, weigh, and count the gross alpha and gross beta activities in an internal proportional counter.

3B. When the filtration is by membrane filter and the solids range between 5 and 10 mg/cm^2 for alpha counting and 10 to 20 mg/cm^2 for beta counting, place the filter in a tared planchet, flood with alcohol, and ignite in a Bunsen flame.

4B. With aid of a rubber policeman and alcohol (wash bottle) spread the residue uniformly over the entire dish area (20 cm^2).

5B. Dry in an oven, desiccate to constant weight, weigh, and count the gross alpha and gross beta activities in an internal proportional counter.

3C. When the filtration is by cellulose fiber filters, or when the suspended solids exceed the specified limits above, place the filter in a tared planchet or crucible, and ignite.

4C. Transfer the ash to a tared planchet with distilled water with or without a few drops of nitric acid, as necessary.

5C. Dry at 110° C, desiccate to constant weight, weigh, and count the gross alpha and gross beta activities using an internal proportional counter.

Calculations

Gross alpha and gross beta activities of the sample can be reported as activities of the suspended solids per liter of water sample or per gram of dry residue.

$$\text{gross alpha activity* (pCi/liter or mg)} = \frac{A}{B \times C \times D}$$

where A = net alpha count rate (cpm)
B = efficiency for counting alpha activity in a "weightless" sample (cpm/pCi)
C = volume of sample (liters), or weight of residue (mg)
D = correction factor for self-absorption in the sample

$$\text{gross beta activity** (pCi/liter or mg)} = \frac{A}{B \times C \times D}$$

where A = net beta count rate (cpm)
B = efficiency for counting gross beta activity (cpm/pCi)
C = volume of sample (liters), or weight of residue (mg)
D = correction factor for self-absorption in the sample

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* If sample thickness exceeds 10 mg/cm^2, assume infinite thickness and report an approximate gross alpha assay, or repeat the test on a smaller portion of the sample.

** If the sample thickness exceeds 20 mg/cm^2, and ^{90}Sr-^{90}Y self-absorption factors are used, report beta-gamma activity rather than gross beta activity.

GROSS ALPHA AND GROSS BETA ACTIVITY IN SUSPENDED SOLIDS (By Difference)

Some waters, such as waste effluents, may contain a high concentration of material which is difficult or impossible to filter. If the determination of both dissolved and non-filterable gross activities is desired, it is usually more convenient to determine the total residue activity and the dissolved solids activity and obtain the suspended solids activity by difference.

Principle of Method

The total residue is obtained by evaporating the sample to near dryness, transferring the concentrate to a planchet, drying it to constant weight, and counting its gross alpha and gross beta activities. Another measured volume of sample is centrifuged, and the clear water is decanted and processed as a potable water sample for analysis of dissolved solids. Activity of suspended solids is then computed as the difference between the two values.

Reagents

lucite: 0.5 mg/ml in acetone

nitric acid, HNO_3: 3N

Apparatus

internal proportional counter: as described on page 5-8

planchets: corrosion-resistant metal, as described on page 5-8

Procedure

1. Take a subsample with extreme care to assure homogeneous sampling, and pour into a beaker. Evaporate to near dryness.
2. For samples having total residue density thickness of less than 5 mg/cm^2 for alpha counting or less than 10 mg/cm^2 for beta counting, process according to the procedure for GROSS ALPHA AND GROSS BETA ACTIVITY IN TOTAL RESIDUE (page 5-7).
3. In a tared vessel, evaporate a volume of 100 ml or more to near dryness on a hot plate.
4. Dry in an oven at 100° C to constant weight, and weigh.

5. If the dried solids are high in organic material, ignite in a muffle furnace at 550° C for 1-2 hours; then weigh.
6. Powder the fixed solids or dried solids low in organic matter in a mortar with pestle. Spread approximate weights of solids uniformly over the area of a tared, metal planchet with the aid of alcohol or distilled water.
7. Dry in an oven, desiccate to constant weight, weigh, and count the gross alpha and gross beta activity of the solids in an internal proportional counter.
8. Take another subsample with extreme care to assure homogeneous sampling, and place in a centrifuge tube.
9. Centrifuge to obtain a volume of clear water in which to determine the activity of dissolved solids.
10. Determine the activity of dissolved solids by the procedure given in GROSS ALPHA AND GROSS BETA ACTIVITY IN DISSOLVED SOLIDS (page 5-10).

Calculations

Compute the gross alpha and gross beta activities of the total residue and of the dissolved solids as described in the respective procedures (pages 5-11 and 5-14). Then compute the activities in the suspended solids as the difference between the total residue activity and the dissolved solids activity per liter of water.

GROSS ALPHA AND GROSS BETA ACTIVITY IN SUSPENDED AND DISSOLVED SOLIDS
(Alternate Method)

This method is applicable to the determination of gross alpha and/or gross beta activity in dissolved and suspended solids in either fresh or saline water.

Principle of Method

The suspended and dissolved solids are separated by filtration. The conductance of the solution containing the dissolved solids is determined on a purity meter, and a suitable aliquot is taken for analysis. The aliquot is evaporated to a low volume, transferred to a high-wall stainless steel planchet, weighed, and counted for gross alpha and gross beta activities. The suspended solids on the filter are dried, weighed, and separated from the paper by ignition. The residue is counted for gross alpha and gross beta activities.

Reagents

ethyl alcohol, C_2H_5OH: 95%
lucite: 0.5 mg/ml in acetone (plastic spray can be used in place of lucite solution)

Apparatus

Barnstead purity meter
desiccator
Millipore filtering apparatus: 250-ml capacity
Millipore Type HA membrane filter: 0.8-μ pore size, 47-mm diameter
stainless steel, high-wall planchets

Procedure

1. Using suction, filter a 1-liter portion of the well-shaken sample through a tared 47-mm Millipore filter. Retain the filter and precipitate.
2. Pipet 1.0 ml of the filtrate into a 100-ml volumetric flask, dilute to volume with distilled water, and mix thoroughly.
3. Set the temperature control knob on the purity meter at the approximate

temperature of the diluted solution.

4. Determine the conductance of the solution (read as ppm NaCl).
5. Determine the conductance of the distilled water used for dilution, and subtract this reading from the one taken in Step 4.
6. Using the conductance table (Table 5.2-1), determine the aliquot of undiluted filtrate to be used.
7. Evaporate the aliquot on a hot plate to approximately 10 ml.
8. Transfer the evaporated aliquot of filtrate to a tared, 2-inch diameter high-wall, stainless steel planchet. Wash the beaker several times with small portions of distilled water, and add the washings to the planchet.
9. Dry the sample under a heat lamp, cool, weigh, and fix with a thin coat of lucite solution or plastic spray.
10. After at least 6 hours, count the alpha and/or beta activity of the dissolved solids in an internal proportional counter.
11. Dry the filter from Step 1 in a 120° C oven for 1 hour. Cool in a desiccator, weigh, and calculate the amount of suspended solids.
12. Transfer the filter and solids to a 2-inch diameter high-wall, stainless steel planchet.
13. Cover the sample with alcohol, and ignite.
14. Ash the sample and paper over a gas flame. Then cool, and fix the ash with lucite solution or plastic spray.
15. After at least 6 hours, count the alpha and/or beta activity of the suspended solids.

Calculation

Calculations are the same for both dissolved and suspended solids.

$$\text{gross alpha or beta activity (pCi/liter or mg)} = \frac{A}{B \times C \times D}$$

where A = net alpha or beta count rate (cpm)

B = counting efficiency (cpm/pCi)

C = volume of sample (liters), or weight of solids (mg)

D = self-absorption correction factor

Evaluation of Data

If the total beta activity (of both suspended and dissolved solids) exceeds 10 pCi/liter, an analysis for strontium 90 should be made. If the total alpha activity exceeds 3 pCi/liter, analysis of radium 226 is indicated.

Table 5.2-1 Water sample conductance and aliquot volume

CONDUCTANCE RANGE (ppm NaCl)	ALIQUOT VOLUME (ml)
0 - 1.9	1000
2 - 2.2	900
2.3 - 2.4	800
2.5 - 2.7	700
2.8 - 3.5	600
3.6 - 4.4	500
4.5 - 6.4	400
6.5 - 8.4	300
8.5 - 11	200

GROSS BETA ACTIVITY IN SALINE WATER (Basic Sulfide Precipitation)

The high level of dissolved solids in saline water requires the use of special techniques to prevent inaccuracies due to self-absorption in heavy residues on the counting planchet. Use of a sulfide precipitation followed by a carbonate procedure offers a reasonably accurate measurement of gross beta activity in saline water without high residue weight.

Principle of Method

After the sample is acidified and filtered, zinc, nickel, cobalt, iron, and strontium carriers are added to the filtrate. The basic sulfides are precipitated with hydrogen sulfide, filtered, and ignited. The residue is transferred to a planchet and counted for gross alpha and gross beta activities. The filtrate from the sulfide precipitation can be treated for a carbonate precipitation, and the fraction coprecipitated with strontium can be counted for gross beta activity.

Reagents

ammonium hydroxide, NH_4OH: 6N
hydrochloric acid, HCl: 6N
hydrogen sulfide, H_2S: gas
mixed carrier: 22 mg Sr^{+2} per ml, and 5 mg each of Zn^{+2}, Fe^{+3}, Ni^{+2}, and Co^{+2} per ml

Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$
Zn^{+2} as zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$
Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$
Ni^{+2} as nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$
Co^{+2} as cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$

Apparatus

analytical oven
internal proportional counter

Procedure

1. Acidify the entire sample (usually one gallon) with 2 ml 6N HCl. Filter a 1-liter portion of the sample through Whatman No. 12 folded filter paper. Wash filter with approximately 600 ml of warm distilled water. Combine filtrate with wash water.

2. To the filtrate, add 2 ml of mixed carrier. Acidify the solution with 2 ml 6N HCl.
3. Heat solution to boiling. Adjust the pH to 8 with 6N NH_4OH (pH paper).
4. Precipitate sulfides with H_2S gas, stirring vigorously. Continue to stir regularly for 10-15 minutes and digest for 1 hour, maintaining pH 8 with 6N NH_4OH.
5. Cool, filter the solution through a Whatman No. 541 filter paper, and wash the precipitate with approximately 100 ml of hot distilled water. Save the filtrate for further analysis, if desired.
6. Dry, and ignite the precipitate and paper at 550° C for 1 hour.
7. Wash the residue from the ignition crucible into a tared planchet.
8. Dry the residue under an infrared lamp, and weigh. Designate as "basic sulfides". Count the beta activity in an internal proportional counter.

   [Note: The filtrate from the sulfide precipitation (Step 5) can be analyzed for gross beta activity by a basic carbonate method. The filtrate is acidified and boiled to remove excess hydrogen sulfide. Strontium is then precipitated from a basic solution as the carbonate. The carbonate is converted to the nitrate with concentrated HNO_3, the nitrate precipitate is dissolved, and strontium carbonate is precipitated. This precipitate is collected by centrifugation, transferred to a planchet, dried, weighed, and counted for gross beta activity.]

Calculation

$$\text{gross beta activity of basic sulfides (pCi/liter)} = \frac{A}{B \times C \times D}$$

where A = net beta count rate (cpm)

B = counting efficiency for a "weightless" sample (cpm/pCi)

C = volume of sample (liters) or weight of sulfides (mg)

D = correction factor for self-absorption in the sample

References

Cited reference:

1. *Public Health Service Drinking Water Standards — 1962.* Public Health Service Publication No. 956, Washington, U. S. Government Printing Office (1962)

Uncited references:

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

Sodd, V. J., A. S. Goldin, and R. J. Velten. "Determination of radioactivity in saline waters". *Anal Chem 32*:25-26 (1960)

5.2.2 Strontium 89 and Strontium 90

One of the most important elements of mixed fission products contributing to the body burden of beta emitters is radiostrontium (^{89}Sr and ^{90}Sr). The physiological chemistry of strontium is similar to that of calcium, leading to deposition in the hard tissues of the body. Although strontium 89 has a half-life of about 50 days and is relatively transient unless replenished, strontium 90 has a half-life of 28 years and decays to yttrium 90 which has a high beta energy.

The strontium body burden comes principally from food and drinking water, and the fraction of ingested strontium metabolized depends on the available strontium (radioactive and stable) in relation to the available calcium in the total diet(1). Therefore, in assessing the effects of radioactive strontium, account must also be taken of stable strontium, normally present in minute quantities in surface water and most ground water, and the amount of calcium.

Reference

1. Report of the United Nations Scientific Committee on the Effects of Atomic Radiation. General Assembly Official Records, 19th Session, Supplement No. 14 (A/5814) United Nations

OXALATE PRECIPITATION METHOD

Radiostrontium in drinking water and in clear water having a moderate amount of other radioactive elements is separated from sample water by oxalate precipitation. The calcium, barium, radium, and rare earth nuclides in the precipitate are separated as soluble nitrates, while radiostrontium is precipitated as strontium nitrate in concentrated nitric acid. Although the radiostrontium from the nitrate purification step could be immediately mounted and counted for the beta activity of total radiostrontium, this is an estimate useful only as a screening test. It is usually more expedient to allow yttrium 90 to grow in to the strontium for seven to fourteen days and then separate the yttrium 90 from the strontium. Yttrium 90 is measured to estimate the strontium 90, and the combined strontium 89 and 90 activity is measured so that the strontium 89 can be estimated by difference.

Principle of Method

The acidified sample of clear water with stable strontium and calcium carriers is treated with oxalic acid at pH 3.0 to precipitate insoluble oxalates. The oxalates are dissolved in nitric acid and strontium nitrate is separated from calcium as a precipitate in 70% nitric acid. The residue is purified by adding iron and rare earth carriers and precipitating them as hydroxides. After a second strontium nitrate precipitation from 70% nitric acid, the nitrates are dissolved in water and, with added yttrium carrier, are stored for ingrowth of yttrium 90. The strontium is again precipitated and separated from 70% nitric acid with the yttrium nitrate being in the supernate. Each fraction is precipitated separately as an oxalate and collected on a glass fiber filter or planchet for counting either total radiostrontium or yttrium 90 or both.

Reagents

acetic acid, CH_3COOH: 1.5N
ammonium acetate, $NH_4C_2H_3O_2$: 3N
ammonium acetate buffer: pH 5.0
ammonium hydroxide, NH_4OH: concentrated (15N), 6N, 1N
ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 0.5% w/v
bromcresol green indicator: 0.1% w/v in ethyl alcohol

carrier solutions:

Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 7 mg Ba^{+2} per ml

Ca^{+2} as calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$: 40 mg Ca^{+2} per ml

Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20 mg Sr^{+2} per ml

Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml

hydrochloric acid, HCl: concentrated (12N), 0.5N

hydrogen peroxide, H_2O_2: 30% solution

nitric acid, HNO_3: fuming (90%), concentrated (16N), 6N, 3N

oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: saturated at room temperature

scavenger solution: 20 mg Fe^{+3} per ml, 10 mg each Ce^{+3} and Zr^{+4} per ml

Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$

Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$

Zr^{+4} as zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$

Apparatus

analytical balance
low-background beta counter
medium-porosity filter stick
pH meter

Procedure

1. To 1 liter of acidified clear water in a 2-liter beaker, add 1 ml strontium carrier solution, 1 ml barium carrier solution, and, if necessary, 10 ml calcium carrier solution. (Improved precipitation may be obtained by adding calcium to soft waters.) Stir thoroughly and while stirring add 125 ml saturated oxalic acid solution.
2. Using a pH meter, adjust the pH to 3.0 with 15N NH_4OH, and allow the precipitate to settle for 5-6 hours.
3. Aspirate the supernate through a medium-porosity filter stick. Wash the precipitate and the beaker walls with 0.5% ammonium oxalate while continuing the aspiration.
4. Transfer the precipitate to a 250-ml beaker with 16N HNO_3 and place the filter stick in the beaker. Heat the sample on a hot plate until the precipitate separates from the filter stick. Then use the 16N HNO_3 rinsings of the large beaker to wash the filter stick inside and outside. Collect the washings in the small beaker.

5. Evaporate the solution to near dryness. Then add 50 ml 16N HNO_3 and repeat the acid addition and evaporation until the residue is colorless.

6. Transfer the residue to a 40-ml centrifuge tube, rinsing with a minimum volume of 16N HNO_3. Cool in a refrigerator overnight. Centrifuge at 1500-1800 rpm for 10 minutes, and discard the supernate.

7. Dissolve the precipitate in 5 ml 3N HNO_3 and then add 10 ml fuming nitric acid. Centrifuge, and discard the supernate.

8. Dissolve the precipitate in 5 ml distilled water. Add 3 drops of bromcresol green indicator, and titrate with 6N NH_4OH until the color changes from yellow to blue. Back titrate with 0.5N HNO_3 until the solution barely turns yellow.

9. Add 5 ml ammonium acetate buffer, heat the solution in a water bath, and add 1 ml of 0.25N Na_2CrO_4. Digest until a barium chromate precipitate is formed. Then cool and filter through Whatman No. 42 filter paper into a 250-ml beaker. Wash the precipitate with warm distilled water. Save the precipitate for barium determination (see 5.2.3).

10. To the filtrate add 5 drops of scavenger solution, 2 drops 12N HCl, and 5 drops 30% H_2O_2. Warm, and add 15N NH_4OH a drop at a time until a precipitate forms. Filter through Whatman No. 42 filter paper. After washing the precipitate with 6N NH_4OH, discard it.

11. Evaporate the filtrate to approximately 10 ml and transfer it to a 40-ml centrifuge tube with a minimum volume of 15N NH_4OH. Add 5 ml 15N NH_4OH and 2 ml 3N Na_2CO_3. Mix thoroughly, cool, and centrifuge. Check for completeness of precipitation. When complete, discard the supernate.

12. Dissolve the precipitate in no more than 4 ml of 3N HNO_3. Then add 10 ml fuming HNO_3, cool in a water bath, and centrifuge. Decant and discard the supernate.

13. Repeat Step 12. Then, RECORD THE TIME AND DATE AS THE BEGINNING OF YTTRIUM 90 INGROWTH. If no immediate count of total radiostrontium is desired, add to the precipitate 1 ml yttrium carrier solution and 4 ml 6N HNO_3, and store for 7 to 14 days to allow yttrium 90 to grow in. Then proceed with Step 18.

14. To determine total radiostrontium, dissolve and transfer the strontium nitrate with 10 ml distilled water to a 40-ml centrifuge tube. Add 5 ml 15N NH_4OH and 2 ml 3N Na_2CO_3. Mix thoroughly, cool, and centrifuge.

When precipitation is complete, decant and discard the supernate.

15. Slurry the strontium carbonate precipitate with 15N NH_4OH to a tared glass fiber filter in a filter holder. Filter with suction, wash the carbonate with NH_4OH, dry with suction and a heat lamp. Cool and weigh the precipitate, and count its beta activity as "total radiostrontium" in a low-background beta counter for which the efficiencies for counting ^{89}Sr and ^{90}Sr are known.

    [Note: After 3 to 7 days, the beta activity of total radiostrontium and yttrium 90 can be counted if an early estimate of ^{89}Sr and ^{90}Sr is desired.]

16. Dissolve the strontium carbonate on the filter in 6N HNO_3 and transfer the solution to a 40-ml centrifuge tube. The total volume for dissolution and rinsing should be about 4 ml.
17. Add 1 ml yttrium carrier solution and store until 7 to 14 days have elapsed since Step 13 was completed.
18. To the centrifuge tube containing the strontium-yttrium sample from Step 13 or Step 17, add 15N NH_4OH a drop at a time to the bromcresol green endpoint. Then add 5 ml 15N NH_4OH in excess.
19. Centrifuge. Decant and save the supernate. RECORD THE TIME AS THE END OF YTTRIUM 90 INGROWTH AND THE BEGINNING OF ITS DECAY. Wash the precipitate twice with 20-ml portions of hot distilled water, combining the supernates for determination of strontium carrier recovery (see 5.3.1).
20. Dissolve the precipitate with 3N HNO_3 and repeat Steps 18 and 19.
21. Dissolve the precipitate in 3N HNO_3 (about 4 drops), add 25 ml distilled water, and heat the solution in a water bath at 90° C.
22. Gradually and with stirring, add 15-20 drops of saturated oxalic acid solution followed by 2-3 drops 15N NH_4OH to adjust the pH to 2.0-3.0. Digest the precipitate for 5 minutes; then cool in an ice bath, stirring occasionally.
23. Transfer the precipitate to a two-piece funnel containing a tared glass fiber filter. Allow the precipitate to settle by gravity; then apply suction. Wash the precipitate with hot distilled water; then wash three times with 95% ethyl alcohol and three times with diethyl ether.
24. Dry the precipitate with suction for 2 minutes. Weigh, and mount in an appropriate counting dish.

25. Count the beta activity of yttrium 90 in a low-background beta counter.

Calculations

$$\text{strontium 90 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of strontium carrier

C = efficiency for counting yttrium 90 as yttrium oxalate (cpm/pCi)

D = sample volume (liters)

E = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from decantation of the strontium supernate [Step 19] to the time of counting [Step 25]

F = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from the start of the ingrowth period [Step 13] until the separation of yttrium and strontium [Step 19]

$$\text{strontium 89 activity (pCi/liter)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G \times H + I \times J)\right]$$

where A = net beta count rate of total radiostrontium (cpm)

B = counter efficiency for counting strontium 89 as strontium carbonate (cpm/pCi)

C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting [Step 15]

D = recovery of strontium carrier [Step 19]

E = sample volume (liters)

F = strontium 90 activity (pCi/liter)

G = self-absorption correction factor for counting radiostrontium as strontium carbonate, obtained by comparing the density thickness of the sample (mg/cm^2) with a self-absorption calibration curve

H = counter efficiency for counting strontium 90 as strontium carbonate (cpm/pCi)

I = counter efficiency for counting yttrium 90 as yttrium oxalate (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from decantation of the yttrium nitrate supernate [Step 12] to the time of counting

References

Division of Radiological Health. *Radionuclide Analysis of Environmental Samples, A Laboratory Manual of Methodology.* U. S. Department of Health, Education, and Welfare, Public Health Service, R. A. Taft Sanitary Engineering Center, Technical Report R59-6, Cincinnati (revised 1966)

Goldin, A. S., R. J. Velten, and G. W. Frishkorn. "Determination of radioactive strontium". *Anal Chem 31*:1490-1492 (1959)

Murthy, G. K., L. P. Jarnagin, and A. S. Goldin. "A method for the determination of radionuclides in milk ash". *J Dairy Sci 42*:1276-1287 (1959)

TRIBUTYL PHOSPHATE EXTRACTION METHOD (Strontium 90)

Clarified water samples are analyzed for strontium 90 by a technique which is specific in eliminating interferences from relatively fresh mixed fission products in samples of high solids content. Monovalent salts remain with the sample water when the alkaline earths with carriers are precipitated as carbonates. Calcium and magnesium are separated by precipitating strontium nitrate in fuming nitric acid, and the yttrium which has grown in is extracted with tributyl phosphate. Just as in the OXALATE PRECIPITATION METHOD, fractions can be isolated for estimating the amount of strontium 89 and of barium 140.

Principle of Method

The alkaline earths, including rare earths and carrier strontium and barium, are precipitated as carbonates from a hot sample in basic solution. The strontium is dissolved in nitric acid, then separated from calcium and radioelement interference by fuming nitric acid precipitation of strontium nitrate. The strontium residue is stored to allow yttrium 90 to grow in from strontium 90. The yttrium is then extracted into tributyl phosphate, back-extracted into dilute nitric acid, and evaporated in a planchet for counting.

Reagents

ammonium acetate buffer: pH 5.0

ammonium hydroxide, NH_4OH: concentrated (15N), 6N

carrier solutions:

- Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 7 mg Ba^{+2} per ml
- Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20 mg Sr^{+2} per ml
- Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml

diethyl ether, $(C_2H_5)_2O$: anhydrous

ethyl alcohol, C_2H_5OH: absolute (100%)

nitric acid, HNO_3: fuming (90%), 6N, 3N, 0.1N

oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N

sodium carbonate, Na_2CO_3: 3N

sodium chromate, Na_2CrO_4: 3N

sodium hydroxide, NaOH: 6N

scavenger solution: 20 mg Fe^{+3} per ml, 10 mg each Ce^{+3} and Zr^{+4} per ml

Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$

Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$

Zr^{+4} as zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$

tri-*n*-butyl phosphate [TBP]: pre-equilibrated with $14\underline{N}$ HNO_3

Apparatus

low-background beta counter

membrane filters: Millipore Type HA (Millipore Filtration Corp., Bedford, Mass.) or equivalent

separatory funnels, 60-ml capacity

suction-filtration apparatus: Pyrex Hydrosol Microanalysis Filter Holder (Millipore Filtration Corp.) or equivalent

Procedure

1. To 1 liter of clear water in a 2-liter beaker, add 1.0 ml of strontium carrier and 3 ml of barium carrier. Stir, and heat to near boiling on a hot plate.
2. Adjust pH to 10 (pH paper) with about 10 ml $6\underline{N}$ NaOH and add 30 ml of $3\underline{N}$ Na_2CO_3, with stirring. Continue heating until precipitate settles to the bottom of the beaker. Remove beaker from hot plate and cool to room temperature.
3. Decant the supernate to waste. Using $0.1\underline{N}$ Na_2CO_3 in a wash bottle, transfer the precipitate to a 40-ml graduated centrifuge tube. Centrifuge, and discard the supernate. Add 20 ml $0.1\underline{N}$ Na_2CO_3 to the residue. Stir, centrifuge, and discard the supernate.
4. Dissolve the residue in 8 ml $3\underline{N}$ HNO_3. Add 20 ml fuming HNO_3, with stirring. Cool in an ice bath for 10 minutes. Centrifuge, and discard the supernate.
5. Repeat Step 4.
6. Dissolve the nitrate precipitate in 20 ml distilled water. Add 1 ml scavenger solution and adjust the pH to 7 (pH paper) with $6\underline{N}$ NH_4OH. Heat, centrifuge, and decant the supernate. Discard the residue.
7. Add 5 ml ammonium acetate buffer and heat in a water bath. With $6\underline{N}$ NH_4OH or $6\underline{N}$ HNO_3, adjust the pH to 5.0 using pH paper. Heat the solution in a water bath, and add 1 ml $3\underline{N}$ Na_2CrO_4 dropwise, with

stirring, to precipitate barium chromate. Centrifuge, and decant the supernate into a clean 40-ml centrifuge tube. Save the residue for barium 140 analysis, if desired (see 5.2.3).

8. Add 5 ml 3N Na_2CO_3 to precipitate strontium carbonate. Stir, and after a few minutes centrifuge and check the supernate for completeness of precipitation with a few drops of 3N Na_2CO_3. Decant the supernate to waste. Wash the residue with 20 ml 0.1N Na_2CO_3. Centrifuge, and decant the supernate to waste.
9. Dissolve the residue in 8 ml 3N HNO_3. Add 20 ml of fuming HNO_3, and stir. Cool the mixture in an ice bath for 10 minutes. Centrifuge, and decant the supernate to waste. Invert the tube on paper towels to drain dry. RECORD TIME OF DECANTATION AS THE BEGINNING OF YTTRIUM 90 INGROWTH. Store the strontium nitrate residue for one to two weeks to allow yttrium 90 to grow in.
10. Add 1.0 ml of yttrium carrier and 3.0 ml 3N HNO_3 to the centrifuge tube. Warm gently to dissolve the residue.
11. Add 10 ml of fuming HNO_3, and stir. Cool in an ice bath for 10 minutes. Centrifuge, and decant the supernate into a 60-ml separatory funnel labeled SF-1.
12. Dissolve the residue in 4 ml 3N HNO_3; then add 10 ml fuming HNO_3. Stir, and cool in an ice bath for 10 minutes. Centrifuge, and decant the supernate into SF-1. Drain excess HNO_3 from the centrifuge tube by inverting tube on a paper towel and save the strontium nitrate residue for strontium 89 and strontium recovery determinations.
13. Add 4 ml of distilled water to SF-1 to make the solution 14N in nitric acid. Add 10 ml of TBP and shake for 5 minutes. Allow phases to separate; then drain the acid phase into a 60-ml separatory funnel labeled SF-2.
14. Add 10 ml of TBP to SF-2, and shake for 5 minutes. Allow phases to separate; then drain off the acid phase into a clean separatory funnel labeled SF-3.
15. Drain the organic phase from SF-2 into SF-1.
16. Add 10 ml TBP to SF-2, shake to rinse, and drain the rinsings into SF-3.
17. Shake SF-3 for 3 minutes. Allow the phases to separate; then drain the acid phase into SF-2 and drain the organic (TBP) phase into SF-1.

Combine the acid phases in SF-2 and SF-3, and save for strontium 89 and strontium recovery determination.

18. Add 10 ml distilled water to the three 10-ml TBP extracts in SF-1. Shake 5 minutes, allow the phases to separate, and drain the organic phase into a clean separatory funnel labeled SF-4. Transfer the aqueous phase into a 40-ml centrifuge tube labeled CT-1.
19. Add 10 ml 0.1N HNO_3 to SF-4, shake 3 minutes, and allow the phases to separate. Drain the TBP phase into SF-1 and the aqueous phase into CT-1.
20. Add 10 ml 0.1N HNO_3 to SF-1, and shake for 3 minutes. Allow phases to separate. Drain the acid phase into CT-1 and the TBP phase to waste.
21. To the combined yttrium nitrate extracts in CT-1, add 5 ml of 2N oxalic acid and using a pH meter, adjust the pH to 1.5 with about 2 ml 15N NH_4OH. Stir and cool in an ice bath for approximately 20 minutes. Centrifuge, and discard the supernate.
22. Weigh a planchet and a 2.5-cm diameter membrane filter. Place the membrane filter into the filtering apparatus.
23. Slurry the precipitate onto the membrane with 10 ml of cold distilled water, and filter with vacuum. Wash the precipitate with one 10-ml portion of cold distilled water, using the water to wash out the centrifuge tube. Dry the precipitate with three 20-ml portions of absolute ethyl alcohol and three 10-ml portions of diethyl ether. Continue suction for 2 minutes.
24. Transfer membrane filter and precipitate to a tared stainless steel planchet, and weigh after a delay of 10-15 minutes.

    [Note: Calculate the recovery of yttrium carrier by comparing the weight of the precipitate with that obtained by precipitating yttrium oxalate from 10 ml of yttrium carrier solution, following Steps 21-25.]
25. Count the yttrium oxalate precipitate in a low-background beta counter to determine the yttrium 90 activity. Make sure that the filter remains centered in the planchet during counting. Count again after 3 days to confirm that yttrium 90 is not contaminated by other radionuclides.

Calculation

$$\text{strontium 90 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F \times G}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of strontium carrier [Step 12]

C = recovery of yttrium carrier [Step 24]

D = efficiency for counting yttrium 90 as yttrium oxalate mounted on a 2.5-cm membrane filter (cpm/pCi)

E = sample volume (liters)

F = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from the decantation of the yttrium 90 supernate to the time of counting

G = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from the start of the ingrowth period until the time of decantation of the yttrium 90 supernate [Step 11]

Reference

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

DIFFERENCE METHOD (Strontium 89)

In the concentration and purification of strontium from fresh water and saline water samples, analyses 3.2.5, the sequential determination of total strontium allows for a measurement of strontium 89 by the DIFFERENCE METHOD. This calculation assumes that strontium 85 is not present or its concentration is known by gamma spectrometry and that the only other radioelement is strontium 90 which has been determined previously.

Principle of Method

The purified strontium isotopes which have been set aside during the analysis of strontium 90 are separated from ingrown yttrium by precipitating strontium nitrate from 17N nitric acid. The precipitate is dissolved and reprecipitated from ammoniacal solution as an oxalate.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N)
ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 1N
diethyl ether, $(C_2H_5)_2O$: anhydrous
ethyl alcohol, C_2H_5OH: absolute (100%)
nitric acid, HNO_3: fuming (90%), 3N
sodium carbonate, Na_2CO_3: 3N

Apparatus

low-background beta counter
membrane filters: Millipore Type HA (Millipore Filtration Corp., Bedford, Mass.) or equivalent
suction-filtration apparatus: Pyrex Hydrosol Microanalysis Filter Holder (Millipore Filtration Corp.) or equivalent

Procedure

1. Evaporate to near dryness the combined acid in SF-2 and SF-3 (Step 17 of the TRIBUTYL PHOSPHATE EXTRACTION METHOD for ^{90}Sr). Neutralize the residual solution with 15N NH_4OH and transfer it to a 40-ml centrifuge tube. Add 5 ml excess 15N NH_4OH and 2 ml 3N Na_2CO_3. Mix

thoroughly; then cool. If there is a precipitate of strontium carbonate, centrifuge the sample, and decant the supernate to waste.

2. Dissolve the residue in 2 ml 3N HNO_3 and transfer, using 2 ml 3N HNO_3 for the rinse, to the strontium nitrate residue saved from Step 12 of the TRIBUTYL PHOSPHATE EXTRACTION METHOD.
3. Add 10 ml fuming HNO_3, stir, cool in an ice bath, centrifuge, and decant the supernate to waste. RECORD THE TIME OF DECANTATION AS THE BEGINNING OF YTTRIUM 90 INGROWTH.
4. Dissolve the nitrate precipitate in 10 ml distilled water and add 3 ml 15N NH_4OH. Heat to near boiling in a hot water bath and add 5 ml 1N ammonium oxalate. Cool in an ice bath, centrifuge, and decant the supernate to waste.
5. Weigh a 2.5-cm diameter membrane filter with a stainless steel planchet. Mount the filter in the filtering apparatus.
6. Slurry the strontium oxalate precipitate into the filter funnel, and filter with suction. Wash the precipitate with three 10-ml cold distilled water rinsings of the centrifuge tube. With suction, dry the precipitate with three 10-ml portions absolute ethyl alcohol and three 10-ml portions diethyl ether. Air dry with suction for 2 minutes.
7. Transfer the filter and filter cake to the tared stainless steel planchet and weigh to determine strontium carrier recovery. [Note: Remember the precipitate represents carrier plus sample strontium.]
8. Count the beta activity in a low-background beta counter to determine total radiostrontium and calculate the strontium 89 activity by deducting that part of the count due to strontium 90 (determined in the TRIBUTYL PHOSPHATE EXTRACTION METHOD).

Calculation

$$\text{strontium 89 activity (pCi/liter)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G\times H + I\times J)\right]$$

where A = net beta count rate of total radiostrontium (cpm)

B = counter efficiency for counting strontium 89 as strontium carbonate (cpm/pCi)

C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting [Step 8]

D = recovery of strontium carrier [Step 7]

E = sample volume (liters)

F = previously calculated strontium 90 concentration (pCi/liter)

G = self-absorption factor for counting strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter

H = counter efficiency for counting strontium 90 as strontium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

I = counting efficiency for yttrium 90 as yttrium oxalate mounted on a 2.5-cm diameter membrane filter (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from decantation of the yttrium nitrate supernate [Step 9 of the TRIBUTYL PHOSPHATE EXTRACTION METHOD] to the time of counting

References

Goldin, A. S., R. J. Velten, and G. W. Frishkorn. "Determination of radioactive strontium". *Anal Chem 31*:1490-1492 (1959)

Murthy, G. K., L. P. Jarnagin, and A. S. Goldin. "A method for the determination of radionuclides in milk ash". *J Dairy Sci 42*:1276-1287 (1959)

BASIC CARBONATE METHOD FOR SALINE WATER

The basic carbonate procedure is applicable to saline or fresh water. It is generally performed as part of a strontium 90 analysis.

Principle of Method

Carrier strontium is added and magnesium is removed by precipitation with 8-hydroxyquinoline solution. Strontium is then precipitated as the carbonate, converted to the nitrate and purified by hydroxide scavenging. Strontium carbonate is then counted in a low-background beta counter to determine its activity.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N), 6N
carrier solution:
  Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 88 mg Sr^{+2} per ml
8-hydroxyquinoline, HOC_9H_6N: 7.5% v/v in methanol
nitric acid, HNO_3: fuming (90%), concentrated (16N), 6N, 3N
scavenger solution: 20 mg Fe^{+3} per ml, 10 mg each Ce^{+3} and Zr^{+4} per ml
  Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$
  Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$
  Zr^{+4} as zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$
sodium carbonate, Na_2CO_3: 3N
sodium hydroxide, NaOH: 6N

Apparatus

analytical oven
infrared lamp
low-background beta counter

Procedure

1. Place a 1-liter sample in a 1500-ml beaker.
2. Add 1.0 ml of strontium carrier solution.
3. Heat to near boiling and add 10 ml 6N NH_4OH.
4. While stirring, add 100 ml of 7.5% 8-hydroxyquinoline solution, and allow the precipitate to settle for at least 15 minutes.

5. Using a Buchner funnel, filter through a double layer of Whatman No. 42 filter paper.
6. Wash the precipitate with three 50-ml aliquots of distilled water.
7. Transfer the filtrate to a 1500-ml beaker and add 30 ml 6N NaOH. Heat to near boiling.
8. While stirring, slowly add 50 ml 3N Na_2CO_3.
9. Allow the precipitate to settle. Decant and discard most of the supernate.
10. Transfer the precipitate and remaining supernate into a 250-ml centrifuge bottle. Centrifuge and discard the supernate.
11. Wash the precipitate with 100 ml distilled water. Centrifuge, and decant the supernate to waste.
12. Place the centrifuge bottle containing the precipitate in an oven at a temperature of 105° C. Allow the precipitate to dry overnight.
13. Remove the centrifuge bottle from the oven, allow the precipitate to attain room temperature, and break it up with a stirring rod.
14. While stirring, cautiously add three 10-ml aliquots of 16N HNO_3.
15. Place the centrifuge bottle in a hot water bath, and while heating, stir to aid development of the precipitate.
16. Cool in an ice bath, stirring occasionally.
17. Centrifuge, and discard the supernate.
18. Add 30 ml 16N HNO_3, and repeat Steps 15 through 17.
19. Dissolve the precipitate in 5 ml distilled water, and transfer the solution into a 50-ml centrifuge tube.
20. Rinse the centrifuge bottle with two additional 5-ml portions of distilled water and transfer the washings to the centrifuge tube.
21. Add 1.0 ml of scavenger solution. While stirring, add a few drops of 15N NH_4OH until the mixture is alkaline. Digest in a hot water bath for 10 minutes.
22. Centrifuge, and decant the supernate into a clean 50-ml centrifuge tube.
23. Repeat Steps 21 and 22 once.

    [Note: The rare earth scavenge is carried out to insure the separation of strontium and yttrium.]
24. Add sufficient 3N Na_2CO_3 for complete precipitation of strontium carbonate.

25. Evaporate the solution to about 10 ml and transfer it quantitatively to a planchet using small portions of $0.1\underline{N}$ HNO_3. Evaporate the solution in the planchet to dryness under an infrared lamp.
26. Determine the activity of total radiostrontium in a low-background beta counter.

Calculation

$$\text{total radiostrontium activity (pCi/liter)} = \frac{A}{B \times C \times D}$$

where A = net beta count rate of total radiostrontium (cpm)

B = efficiency for counting total radiostrontium as strontium carbonate (cpm/pCi)

C = sample volume (liters)

D = self-absorption correction for counting radiostrontium as strontium carbonate, obtained by comparing the density thickness of the sample (mg/cm^2) with a self-absorption calibration curve

Reference

Division of Radiological Health. *Radionuclide Analysis of Environmental Samples, A Laboratory Manual of Methodology.* U. S. Department of Health, Education, and Welfare, Public Health Service, R. A. Taft Sanitary Engineering Center, Technical Report R59-6, Cincinnati (revised 1966)

RADIOSTRONTIUM IN SALINE WATER (Alternate Method)

This procedure is designed to follow the analysis of gross beta activity in saline water by basic sulfide precipitation as given in 5.2.1, page 5-20. Strontium 90 and total radiostrontium are separated in the sequential analysis of saline water by an alternate basic carbonate method.

Principle of Method

The supernate from the separation of insoluble sulfides is treated with 8-hydroxyquinoline for the removal of magnesium and then with sodium carbonate in basic solution for the separation of carrier and radiostrontium. The carbonates are further purified and then counted for the beta activity of total radiostrontium. Strontium 90 may be determined by yttrium 90 analysis, and strontium 89 may be calculated as the difference between total radiostrontium and strontium 90 activities.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N), 6N
8-hydroxyquinoline: 7.5% v/v in methanol
methyl orange indicator: 0.1% w/v
nitric acid HNO_3: fuming (90%), concentrated (16N)
scavenger solution: 20 mg Fe^{+3} per ml, 10 mg each Ce^{+3} and Zr^{+4} per ml
  Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$
  Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$
  Zr^{+4} as zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$
sodium carbonate, Na_2CO_3: 3N
sodium hydroxide, NaOH: 6N

Apparatus

analytical oven

Procedure

1. Place in a 1500-ml beaker the supernate obtained from a 1-liter sample in Step 5 of the Basic Sulfide Precipitation method given in 5.2.1. Add 16N HNO_3 dropwise to the methyl orange endpoint. Heat to boiling on a hot plate to expell H_2S, and then add 10 ml 6N NH_4OH.

2. While stirring, add 100 ml of 8-hydroxyquinoline solution and allow the precipitate to settle for at least 15 minutes.
3. Filter through a double layer of filter paper in a Buchner funnel.
4. Wash the precipitate with three 50-ml portions of distilled water.
5. Transfer the filtrate to a 1500-ml beaker, and add 30 ml $6\underline{N}$ NaOH. Heat to near boiling.
6. While stirring, slowly add 50 ml $3\underline{N}$ Na_2CO_3.
7. Allow the precipitate to settle, and decant the clear supernate to waste.
8. Transfer the residue into a 250-ml centrifuge bottle labeled CB-1. Centrifuge, and decant the supernate to waste.
9. Add 100 ml distilled water, and stir. Centrifuge, and decant the supernate to waste.
10. Dry the precipitate in CB-1 overnight in an oven at 105° C.
11. Cool the precipitate to room temperature and break it up with a stirring rod. While stirring, slowly and cautiously add 30 ml $16\underline{N}$ HNO_3.
12. Digest the sample in a hot water bath, stirring occasionally.
13. Cool in an ice bath. Centrifuge, and decant the supernate to waste.
14. Dissolve the residue in 5 ml distilled water. Add 15 ml fuming HNO_3, and repeat Steps 12 and 13.
15. Dissolve the residue in 5 ml distilled water and transfer it to a 40-ml centrifuge tube labeled CB-2.
16. Rinse CB-1 with two 5-ml portions of distilled water and add the rinsings to CB-2.
17. Add 1.0 ml of scavenger solution to CB-2 and stir while adding enough drops of $15\underline{N}$ NH_4OH to make the solution alkaline. Set the bottle in a hot water bath for 10 minutes.
18. Centrifuge, and decant the supernate into a clean 40-ml centrifuge tube. Discard the residue.
19. Repeat Steps 17 and 18.

    [Note: The double hydroxide precipitation completely removes yttrium and rare earth radionuclides.]
20. To the supernate from Step 19, add sufficient $3\underline{N}$ Na_2CO_3 for complete precipitation of strontium carbonate.
21. Continue analysis for total radiostrontium and strontium 90 by following Steps 15 to 25 of the OXALATE PRECIPITATION METHOD, page 5-27.

Calculations

$$\text{strontium 90 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F}$$

where A = net beta count rate of yttrium 90 (cpm)

B = recovery of strontium carrier

C = efficiency for counting yttrium 90 as yttrium oxalate (cpm/pCi)

D = sample volume (liters)

E = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from decantation of the strontium supernate [Step 19] to the time of counting [Step 25]

F = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from the start of the ingrowth period [Step 13] until the separation of yttrium and strontium [Step 19]

$$\text{strontium 89 activity (pCi/liter)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G \times H + I \times J)\right]$$

where A = net beta count rate of total radiostrontium (cpm)

B = counter efficiency for counting strontium 89 as strontium carbonate (cpm/pCi)

C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting [Step 15]

D = recovery of strontium carrier [Step 19]

E = sample volume (liters)

F = strontium 90 activity (pCi/liter)

G = self-absorption correction factor for counting radiostrontium as strontium carbonate, obtained by comparing the density thickness of the sample (mg/cm^2) with a self-absorption calibration curve

H = counter efficiency for counting strontium 90 as strontium carbonate (cpm/pCi)

I = counter efficiency for counting yttrium 90 as yttrium oxalate (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium 90 ingrowth period, where t is the time from decantation of the yttrium nitrate supernate [Step 12] to the time of counting

Reference

Division of Radiological Health. *Radionuclide Analysis of Environmental Samples, A Laboratory Manual of Methodology.* U. S. Department of Health, Education, and Welfare, Public Health Service, R. A. Taft Sanitary Engineering Center, Technical Report R59-6, Cincinnati (revised 1966)

5.2.3 Radiobarium

Barium 140 is one of the more abundant radioelements in mixed fission products. It is a beta emitter having a radioactive half-life of 12.7 days and decays to lanthanum 140, a beta-gamma emitter which decays with a half life of 40.2 hours emitting gamma photons of various energies. The most useful energy for gamma spectral analysis of barium-lanthanum 140 is the 1.60 Mev photon of lanthanum 140.

Upon ingestion from food or water by dairy animals, barium 140, like calcium and strontium, appears in milk as does the lanthanum 140 daughter, presumably from barium 140 decay after ingestion. The determination of radiobarium may be by the non-destructive means of gamma spectrometry in which the lanthanum 140 daughter is measured and assumed to be in equilibrium with the barium 140 parent.

An alternate method is to chemically isolate the barium from other radionuclides and count its beta activity. Verification of the identity and purity of the radionuclide in the barium precipitate can be made by storing the sample and recounting it at intervals to follow the ingrowth of lanthanum 140.

BASIC CARBONATE METHOD

This procedure is designed to be compatible with the OXALATE PRECIPITATION METHOD or the TRIBUTYL PHOSPHATE EXTRACTION METHOD for radiostrontium given in 5.2.2. It can be used to analyze barium 140 in any water sample by adding the appropriate carriers and treating the sample to the point of barium chromate precipitation.

Principle of Method

The alkaline earths with strontium and barium carriers are precipitated as carbonates. The residue is dissolved in dilute nitric acid and then precipitated from 70 percent nitric acid. The nitrates of strontium, barium, radium, and traces of rare earth elements are then dissolved in water, and the rare earths are precipitated as hydroxides. The supernate is then digested with sodium chromate in a solution buffered at pH 5.0 to precipitate barium and radium. Barium is separated from radium and its beta activity is counted.

Reagents

ethyl alcohol, C_2H_5OH: absolute (100%)
hydrochloric acid, HCl: concentrated (12N)
hydrochloric acid — diethyl ether, HCl — $(C_2H_5)_2O$: 5:1 v/v solution

Apparatus

analytical oven
desiccator
low-background beta counter
suction-filtration apparatus: Pyrex Hydrosol Microanalysis Filter Holder (Millipore Filtration Corp., Bedford, Mass.) or equivalent

Procedure

1. Follow the precedure for the OXALATE PRECIPITATION METHOD through Step 9 or the TRIBUTYL PHOSPHATE EXTRACTION METHOD through Step 7 (see 5.2.2).
2. Add approximately 5 ml 12N HCl to the barium chromate precipitate obtained from either procedure. Heat in a water bath until the yellow barium chromate precipitate [$BaCrO_4$] is dissolved and only a white granular barium chloride precipitate [$BaCl_2 \cdot 2H_2O$] remains. The solution will have a green color from the chromic ion [Cr^{+3}].
3. Cool in an ice bath, and add 20 ml cold HCl-diethyl ether reagent. Stir, centrifuge, and decant the supernate. A pure white barium chloride [$BaCl_2 \cdot 2H_2O$] precipitate should remain. If it is not white, repeat the HCl-diethyl ether application. RECORD THE TIME OF FINAL DECANTATION AS THE BEGINNING OF LANTHANUM 140 INGROWTH.
4. Weigh a stainless steel planchet with a 2.4-cm diameter Whatman No. 542 filter paper. Place the filter paper into the suction-filtration apparatus.
5. Transfer the precipitate onto the filter paper using several 10-ml

portions of cold absolute ethyl alcohol. Use at least 30-40 ml of absolute ethyl alcohol.

6. Transfer the filter paper with the precipitate to the tared planchet and dry in an oven at 103° C for at least one hour. Cool in a desiccator for 10-15 minutes; then weigh. Calculate the recovery of barium carrier as barium chloride, and count the precipitate on the planchet in a low-background beta counter. RECORD THE TIME AND DATE OF COUNTING LANTHANUM 140.

Calculation

$$\text{barium 140 activity (pCi/liter)} = \frac{A}{[B \times C \times D][E + (1.15 \times F \times G)]}$$

where A = net beta count rate (cpm)

B = sample volume (liters)

C = barium carrier recovery

D = correction factor $e^{-\lambda t}$ for barium 140 decay, where t is the time in hours from collection of the sample to the time of counting

E = efficiency for counting barium 140 as barium chloride mounted on a 2.4-cm diameter filter (cpm/pCi)

F = efficiency for counting lanthanum 140 in the chloride precipitate mounted on a 2.4-cm diameter filter (cpm/pCi)

G = correction factor $1-e^{-0.015t}$ for the degree of equilibrium attained, where t is the time in hours from the barium separation to the time of counting

1.15 = the ratio of lanthanum 140 activity to barium 140 activity when the mixture is in transient equilibrium. It is obtained by reducing the terms in the "ingrowth equation" for transient equilibrium when barium 140 is corrected for decay from the time of sample collection to the time of lanthanum 140 separation.

Evaluation of Data

If a complete separation of barium from radium is not obtained, the net count rate of the barium chloride precipitate will be high due to the alpha activity of the impure sample. Alpha activity of the sample should be determined separately and the net count rate of the precipitate should be corrected for alpha interference to determine the net count rate of beta activity needed for the calculation of barium 140 activity.

5.2.4 Radium

When gross alpha activity in drinking water exceeds 3 picocuries per liter, the sample is analyzed for radium. The two principal methods employed are: 1) precipitation and purification of radium with barium as the sulfate and counting the alpha activity of the precipitate, and 2) separation of radon from a concentrate of radium in the sample and counting the alpha activity of radon 222.

The first method is a screening technique in which no discrimination between radium nuclides is obtained. It is particularly applicable to drinking water and as long as the concentration of total radium is less than the drinking water standard, examination by a more specific method is unnecessary.

The second method is specific for radium 226 by radon 222 emanation. Radium 226, as well as radium 228, is one of the more important nuclides in causing internal radiation exposure.

TOTAL RADIUM (Precipitation Method)

This screening technique is applicable to drinking water or to any water sample containing only traces of insoluble matter. Although all radium isotopes will be detected if present, the probability of including significant amounts of radium isotopes other than radium 226 in an analysis of drinking water is low. These other isotopes are more apt to occur in industrial wastes from the mining and milling of uranium and thorium. To discriminate between radium 226 and other radium nuclides, the precipitation method and the radon 222 emanation method must be preformed on the same sample.

Principle of Method

Barium carrier is added to the water sample and radium is coprecipitated with barium sulfate from solution containing ethylenediamine tetraacetate.

The precipitate is converted to the carbonate which is then dissolved in nitric acid. Radium daughter products are extracted from this solution into thenoyltrifluoroacetone. Barium sulfate is reprecipitated, weighed for determination of carrier recovery, and counted for total radium alpha activity.

Reagents

ammonium acetate buffer: pH 4.6

ammonium sulfate, $(NH_4)_2SO_4$: 50% w/v

carrier solution:

  Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml

disodium ethylenediamine tetraacetate [EDTA], $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$: 10% w/v

nitric acid, HNO_3: concentrated (16N)

sodium carbonate, Na_2CO_3: 3N

sulfuric acid, H_2SO_4: 2N

2-thenoyltrifluoroacetone [TTA]: 10% w/v in benzene

Apparatus

desiccator

heat lamp (infrared)

internal proportional alpha counter

magnetic stirrer

pH meter

separatory funnel: 60-ml capacity

Procedure

1. To a 250-ml water sample in a 400-ml beaker add 2 ml 50% ammonium sulfate, 20 ml 10% EDTA, and 1.0 ml of barium carrier solution. Adjust the pH to 4.6 using a pH meter. Mix for 5 minutes with a magnetic stirrer.
2. Allow the precipitate to settle, and decant or aspirate the supernate to waste. Using a wash bottle of distilled water, transfer the precipitate to a 40-ml centrifuge tube and dilute to 40 ml. Mix the contents; then centrifuge, and decant the supernate to waste.
3. Add 25 ml 3N Na_2CO_3 to the precipitate. Heat in a water bath for 10 minutes, stirring occasionally. Centrifuge, and decant the supernate to waste.

4. Dissolve the precipitate in several drops of 16N HNO_3. Using ammonium acetate buffer, transfer the solution to a 60-ml separatory funnel and dilute to about 30 ml with buffer.
   [Note: If the precipitate does not dissolve completely, centrifuge the buffered solution, decant the supernate to a clean separatory funnel, and repeat Step 3 on the precipitate, combining the dissolved precipitates in Step 4.]
5. Add 5 ml TTA reagent to the separatory funnel, and shake for 5 minutes. Transfer the aqueous phase to a 40-ml centrifuge tube.
6. Add several drops of 2N H_2SO_4 to the aqueous solution. Centrifuge, and decant the supernate to waste.
7. Add 40 ml distilled water, and mix. Centrifuge, and decant the supernate to waste.
8. Using a minimum volume of distilled water, transfer the precipitate to a tared counting dish such as a stainless steel planchet. Distribute the precipitate uniformly, and dry under a heat lamp.
9. Cool to room temperature in a desiccator to achieve constant weight. Weigh the precipitate, and count its alpha activity in an internal proportional alpha counter within 24 hours of precipitation.

Calculation

$$\text{total radium activity (pCi/liter)} = \frac{A}{B \times C \times D \times E}$$

where A = net alpha count rate (cpm)
B = sample volume (liters)
C = efficiency for counting alpha activity in the barium precipitate (cpm/pCi)
D = barium recovery, computed by dividing the weight of precipitate obtained in Step 9 by the weight of barium sulfate precipitated from 1 ml of carrier solution
E = correction factor $1-e^{-\lambda t}$ for ingrowth of radium 226 daughters, where t is the time in hours from separation of radium to the time of counting

Evaluation of Data

The calculation of total radium activity corrects for daughter product activity grown in from radium 226 only. If ^{223}Ra or ^{224}Ra are present in the sample, they will be in equilibrium with their daughter products and the calculated value of total radium activity will be high.

Improved sensitivity and precision may be obtained for soft waters by evaporating a larger sample to a volume of about 250 ml as long as the concentrate is not turbid when acidified slightly.

References

Baratta, E. J. and A. C. Herrington. "The determination of isotopic radium". Atomic Energy Commission Report WIN-118 (1960)

Goldin, A. S. "Determination of dissolved radium". *Anal Chem* *33*:406-409 (1961)

Holaday, D. A. *et al.* "Control of radon and daughters in uranium mines and calculations on biologic effects". U. S. Dept. of Health, Education, and Welfare, Public Health Service, Public Health Service Publication No. 494 (1957)

Magno, P. J., E. J. Baratta, and E. Ferri. *Procedures for the Chemical and Radiochemical Analysis of Environmental Samples.* U. S. Department of Health, Education, and Welfare, Public Health Service, Northeastern Radiological Health Laboratory Report No. NERHL-64-1, Winchester (1964)

Rushing, D. E., W. J. Garcia, and D. A. Clark. "The analysis of effluents and environmental samples from uranium mills and of biological samples for radium, uranium, and polonium". *Radiological Health and Safety in Mining and Milling of Nuclear Materials, Vol. II*:187, Vienna, International Atomic Energy Agency (1964)

RADIUM 226 IN DISSOLVED SOLIDS (Emanation Method)

Principle of Method

Barium carrier and barium 133 tracer are added to a sample of clear, slightly acidified water and the radium is coprecipitated with barium sulfate. The precipitate is converted from the sulfate to the carbonate and dissolved in nitric acid. Barium carrier recovery is determined by counting the gamma activity of barium 133. The solution is deemanated and aged for two to four weeks to allow radon 222 to grow in. The solution is again deemanated into an evacuated scintillation cell, and the alpha activity of radon 222 is counted.

Reagents

ammonium hydroxide, NH_4OH: concentrated (15N)
ammonium sulfate, $(NH_4)_2SO_4$: 50% w/v
Ascarite: 20-30 mesh
barium 133 tracer: ~0.02 µCi ^{133}Ba per ml
carrier solution:
  Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
disodium ethylenediamine tetraacetate [EDTA], $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$: 10% w/v
magnesium perchlorate, $Mg(ClO_4)_2$: anhydrous (10-20 mesh)
nitric acid, HNO_3: concentrated (16N)
sodium carbonate, Na_2CO_3: 3N

Apparatus

absorption tube, ~100 mm long, 8-mm inside diameter
gamma scintillation counter
magnetic stirrer
pH meter
plastic container, 25-ml capacity, suitable as a container for counting ^{133}Ba gamma activity on a solid crystal scintillation counter
radon bubbler, illustrated in Figure 4.2.4-2, and associated emanation apparatus as illustrated in Figures 4.2.4-1 and -4
radon counter (alpha scintillation counter)
scintillation cell, illustrated in Figure 4.2.4-3
vacuum pump

Procedure

1. To a 250-ml sample in a 400-ml beaker add 2 ml 50% $(NH_4)_2SO_4$, 20 ml 10% EDTA, 1 ml barium carrier, and 1.0 ml barium 133 tracer solutions. Using a pH meter, adjust the pH to 4.6. Mix for 5 minutes, using a magnetic stirrer.
2. Allow the precipitate to settle, and decant or aspirate the supernate to waste. Transfer the precipitate to a 40-ml centrifuge tube with distilled water and dilute to the 40-ml mark. Mix well. Centrifuge, and discard the supernate.
3. Add 30 ml 3$\underline{N}$ Na_2CO_3 to the precipitate, and heat in a water bath for 30 minutes. Stir frequently. Cool, centrifuge, and discard the supernate.
4. Dissolve the precipitate in 2 ml 16$\underline{N}$ HNO_3. If the precipitate does not dissolve completely with the addition of acid and distilled water, centrifuge the sample and transfer the supernate to a plastic container. Then repeat Steps 3 and 4 on the undissolved residue.
5. When the carbonate is completely dissolved, transfer the solution to the plastic container with distilled water (combining solution, if necessary), and dilute to 25 ml total volume. Measure the activity of barium 133 in a gamma scintillation counter, and calculate the barium recovery by dividing the measured activity of the acid solution by the measured activity of 1 ml of tracer solution in a 25-ml volume.
6. Transfer the solution to a radon bubbler. Open both the upper and lower stopcocks and, using a vacuum pump, deemanate the solution by slowly drawing air through the bubbler for about 2 minutes.
7. Close the lower stopcock and evacuate the bubbler for about 3 minutes. Close the upper stopcock, and RECORD THE TIME. Store the solution for 2 to 4 weeks for radon 222 to grow in.
8. At the end of the storage period, fill the upper half of an absorption tube with magnesium perchlorate and the lower half with Ascarite. Attach the tube to the radon bubbler and then attach the scintillation cell to the tube. Slowly open the lower stopcock of the bubbler, allowing air to pass through the solution into the scintillation cell until the system reaches equilibrium.
9. Close the stopcock of the scintillation cell and RECORD THE TIME. This is the beginning of radon 222 decay and ingrowth of radon 222 daughters.

10. Store the scintillation cell for 2 hours; then measure the alpha activity of the cell in a radon counter. RECORD THE TIME OF COUNTING to determine the correction factor for ingrowth of radon 222 daughter products.

Calculation

$$\text{radium 226 activity (pCi/liter)} = \frac{A}{B \times C \times D \times E \times F}$$

where A = net alpha count rate (cpm)

B = sample volume (liters)

C = efficiency of deemanation and counting*

D = correction factor $1-e^{-\lambda t}$ for radon 222 ingrowth, where t is the time from the first deemanation of radon in Step 7 to the end of the second deemanation [Step 9]

E = recovery of barium carrier

F = correction factor $1-e^{-\lambda t}$ for radon 222 daughter ingrowth [^{222}Rn decay], where t is the time from the end of the second deemanation of radon [Step 9] to the time of counting

References

Ferri, E., P. J. Magno, and L. R. Setter. *Radionuclide Analysis of Large Numbers of Food and Water Samples.* U. S. Department of Health, Education, and Welfare, Public Health Service Publication No. 999-RH-17 (1965)

Goldin, A. S. "Determination of dissolved radium". *Anal Chem 33*:406-409 (1961)

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* Determine the efficiency by introducing a known amount of radium 226 into the bubbler, deemanating before and after a 14- to 21-day storage period, and counting the alpha activity of radon 222 in the scintillation chamber. A decimal percentage efficiency of about 0.8 may be expected.

Magno, P. J., E. J. Baratta, and E. Ferri. *Procedures for the Chemical and Radiochemical Analysis of Environmental Samples.* U. S. Department of Health, Education, and Welfare, Public Health Service, Northeastern Radiological Health Laboratory Report No. NERHL-64-1, Winchester (1964)

Rushing, D. E. *Radium 226 in Water (Total, Suspended, and Dissolved) by Radon De-Emanation.* U. S. Department of Health, Education, and Welfare, Public Health Service, Division of Water Supply and Pollution Control, Colorado River Basin Water Quality Control Project Laboratory, Salt Lake City

Rushing, D. E., W. J. Garcia, and D. A. Clark. "The analysis of effluents and environmental samples from uranium mills and of biological samples for radium, uranium, and polonium". *Radiological Health and Safety in Mining and Milling of Nuclear Materials, Vol. II*:187, Vienna, International Atomic Energy Agency (1964)

RADIUM 226 IN SUSPENDED SOLIDS

Principle of Method

The water sample is filtered through a fine cellulose filter, and the filtered material is dried, ashed, and fused with sodium carbonate in a platinum crucible. The melt is dissolved in hydrochloric acid, barium carrier is added, and silica is removed by filtration. The filtrate is transferred to a radon bubbler and the radium 226 is analyzed by the radon 222 emanation method for dissolved solids.

Reagents

hydrochloric acid, HCl: 4N
sodium carbonate, Na_2CO_3: anhydrous

Apparatus

analytical oven
muffle furnace
platinum crucible
suction-filtration flask

Procedure

1. With gentle suction, filter 50 to 1000 ml of a homogeneous sample through a pre-weighed filter paper (such as Whatman No. 42) using a Buchner funnel. Wash with distilled water, and save the filtrate for analysis of dissolved radium 226.
2. Dry the filter paper containing the suspended solids in an oven at 110° C for one hour. Cool in a desiccator, and weigh the filter and its contents to determine the weight of suspended solids.
3. Place the filter paper in a platinum crucible, and heat in a muffle furnace at 500° C for one hour to burn off the filter paper and any organic material. Cool the residue; then add anhydrous sodium carbonate in the proportion of 3 parts Na_2CO_3 to one part residue. Thoroughly mix the Na_2CO_3 with the residue, and fuse at 900° C.
4. Cool the melt. Carefully dissolve it in 4N HCl, and dilute the solution to about 250 ml with distilled water.
5. Continue the analysis by following the procedure for radium 226 in

dissolved solids (under 5.2.4), considering the dissolved melt as the sample.

Calculation

Follow the calculation given for the Emanation Method of radium 226 analysis in dissolved solids. Radium 226 activity can be based on sample volume as in the calculation given, or on weight of suspended solids as determined in Step 2.

References

Baratta, E. J. and A. C. Herrington. "The determination of isotopic radium". Atomic Energy Commission Report WIN-118 (1960)

Magno, P. J., E. J. Baratta, and E. Ferri. *Procedures for the Chemical and Radiochemical Analysis of Environmental Samples.* U. S. Department of Health, Education, and Welfare, Public Health Service, Northeastern Radiological Health Laboratory Report No. NERHL-64-1, Winchester (1964)

Rushing, D. E., W. J. Garcia, and D. A. Clark. "The analysis of effluents and environmental samples from uranium mills and of biological samples for radium, uranium, and polonium". *Radiological Health and Safety in Mining and Milling of Nuclear Materials, Vol. II*:187, Vienna, International Atomic Energy Agency (1964)

RADIUM 226 IN THE TOTAL SAMPLE

When the water sample contains only traces of suspended matter, the procedure for analyzing radium 226 in dissolved solids by radon 222 emanation should be used. Special treatment to dissolve stubborn precipitates may be needed.

For samples containing an appreciable amount of suspended matter a differentiation between suspended and dissolved activity is usually desired and the sum of radium 226 in the two fractions is the radium 226 in the total sample.

If separate analysis of each fraction is not desired, suspended radium can be separated from dissolved radium by filtration and ignited. The filtrate can be analyzed by the procedure for radium 226 in dissolved solids. The ignited solids are then combined with the insoluble carbonates precipitated in Step 3, page 5-54, and the mixture is fused with sodium carbonate. The dissolved melt is then analyzed for combined radium 226 by the radon emanation procedure employed for analysis of dissolved solids only.

5.2.5 Tritium

The National Center for Radiological Health routinely samples and measures the tritium content of surface waters from streams throughout the United States. The selected streams are located near nuclear facilities where tritium could potentially be released to the environment.

DISTILLATION METHOD

Principle of Method

The water sample is purified by distillation, and a portion of the distillate is transferred to a counting vial containing a scintillation fluid. The contents of the vial are then mixed and counted in a liquid scintillation counter.

Reagents

scintillation medium, dioxane solvent
tritium standard solution: $\sim 10^4$ dpm per ml

Apparatus

condenser, miniature
distillation flask, 50-ml capacity
liquid scintillation counter
polyethylene liquid scintillation counting vials

Procedure

1. Distill a 10-ml to 50-ml water sample just to dryness. Collect the distillate in a small container.
2. Dispense 13.0 ml of the scintillation medium into a polyethylene counting vial. (A burette is convenient.)
3. Add 3.0 ml of the sample distillate to the vial, and mix the contents with gentle swirling. Avoid exposure to direct sunlight and use a minimum of artificial light during sample preparation. Clean the vial walls and do not label them (label the caps) to insure optimum light transmission.

4. Prepare a background sample from distilled water in the same manner (Steps 2 and 3). Use water known to have low tritium content, such as triple-distilled deep sea water or deep well water.
5. Prepare a counting standard, using a tritiated water standard, by following Steps 2 and 3.
6. Place samples and standard in the freezer section of a liquid scintillation counter for at least 30 minutes before counting. Count for 2 to 4 hours, depending on sample activity and instrument sensitivity.

Calculation

$$\text{tritium activity (pCi/liter)} = \frac{1000 \times A}{B \times C}$$

where A = net count rate of tritium (cpm)
B = sample volume (ml)
C = efficiency for counting tritium (cpm/pCi)

Evaluation of Data

The minimun level of detectability of this method is approximately 1.2 nanocuries of tritium per liter of water for a 240-minute count. Improved senistivity can be obtained with more sensitive instrumentation.

References

Chesnutt, M. W., J. C. Drobinski, Jr., and R. H. Gorrie. "Tritium in surface waters, 1964-1965". *Rad Health Data 7*:377 (1966)

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

5.2.6 Gamma Emitters

Surface and drinking water generally contain insufficient gamma emitter activity to be measured directly unless large volumes of sample are concentrated. Even then, a mixture of fission products may be too complex for precise resolution of individual radionuclides. In industrial wastes, however, concentrations may be high enough and fractionation of radioelements may have occurred to a degree to permit effective resolution of some of the more energetic gamma emitters.

Even though the mixture of gamma-emitting nuclides may be too complex for quantitative spectral analysis, gamma spectrometry often provides an extremely useful qualitative examination leading to chemical procedures which will result in quantitative measurement of specific nuclides. The non-destructive nature of gamma spectrometry also makes it a desirable screening technique.

One to 3.5 liters of water can be counted directly in a Marinelli beaker which fits over and surrounds the crystal detector. Improved sensitivity can be obtained by evaporating a large volume of sample to some standard volume. A 1-pint covered plastic container similar to a cottage cheese container is frequently used for samples concentrated to less than 500 milliliters. Any solids in the residue must be uniformly distributed through the sample in order to obtain constant counting geometry.

Geometrical configuration of the sample can be improved to increase sensitivity still further by evaporating the sample to a dry or ignited residue in a small container such as a planchet. Volatility of the radionuclides being analyzed limits the applicability of this method of concentration.

Instrumentation and data processing techniques for gamma pulse height analysis of environmental samples are discussed in 1.1.3 and 1.1.4 of SECTION 1. INSTRUMENTATION.

5.3 DETERMINATION OF STABLE ELEMENTS

5.3.1 Strontium Carrier

Although the stable strontium content of most surface and ground waters is usually less than 0.2 milligram per liter, some ground waters and some waste effluents may have a strontium concentration high enough to interfere with determination of strontium carrier recovery in assays of radiostrontium. Also, the concentration of stable strontium occurring in the sample may be of interest in that it can affect the distribution of radiostrontium in food chains or humans.

Usually, however, a true measure is desired of the strontium carrier recovery exclusive of stable strontium which may be in the untreated sample. This may be obtained by one of several methods: 1) determine the stable strontium in the sample and include it with the added carrier strontium, 2) add strontium 85 to the carrier so that carrier recovery can be based on the gamma assay of strontium 85 in carrier and in the recovered strontium under comparable counting geometry, 3) add enough strontium carrier to make the sample strontium negligible with respect to the carrier strontium.

Stable strontium can be measured by flame photometry or gravimetrically as insoluble carbonates or oxalates. For gravimetric determination, the strontium in a volume of carrier equal to the volume added to the sample is precipitated and treated in a manner identical to the total strontium in the sample. This treatment eliminates any difference in composition of the weighed material.

FLAME PHOTOMETRIC METHOD

The total strontium precipitate obtained in the analysis of radiostrontium is dissolved and diluted to volume. The strontium concentration is determined by the procedure given in 3.3.1 of SECTION 3. MILK.

GRAVIMETRIC METHOD

The gravimetric method for determining strontium carrier recovery has been included in the procedures for analysis of strontium 89 and strontium 90 (see 5.2.2). The weight of strontium precipitated from the sample is compared with the weight of strontium precipitated by identical means from an aliquot of the strontium carrier solution. The fraction recovered, or decimal precentage recovery, equals the weight of strontium precipitate obtained from the sample divided by the weight of an identical precipitate of strontium obtained from an equal volume of carrier, assuming that the weight of strontium naturally occurring in the sample is negligible.

STRONTIUM 85 TRACER METHOD

The strontium 85 tracer method for determining strontium carrier recovery is described for the REFERENCE METHOD for analyzing strontium 90 in milk (see 3.2.1 of SECTION 3. MILK). The strontium carrier solution is labeled with a known amount of strontium 85 tracer. The amount of tracer recovered is determined by counting the gamma activity of the supernatant solution remaining after the precipitation of yttrium. The fractional recovery of tracer is assumed to equal the fractional recovery of carrier strontium.

5.3.2 Calcium

Because calcium plays an important role in the biological uptake of strontium, the ratio of radiostrontium to calcium concentrations in the sample is sometimes desired.

Generally, the calcium content of drinking water from surface supplies is less than 50 milligrams per liter and represents only a small fraction of the total dietary intake. Some hard water, however, may contain calcium concentrations as high as 100 milligrams per liter.

Personal preference often dictates whether a classical gravimetric or titrimetric method will be used for the calcium determination(1). The longer time required for the gravimetric measurement may restrict it to occasional use. The permanganate titration method is often preferred when a large number of samples are to be analyzed simultaneously. The rapidity and simplicity of the ethylenediamine tetraacetic acid method(2) makes it suitable for routine control applications. Whatever method is used, care should be taken to re-dissolve any calcium carbonate which may have precipitated during storage of the sample.

EDTA TITRATION

Principle of Method

A sample of water is adjusted to pH 12-13 with sodium hydroxide, and the resulting solution is titrated with disodium ethylenediamine tetraacetate, using Cal-Red as the indicator.

Reagents

Cal-Red indicator*: 1% w/v

calcium standard solution, $CaCO_3$: 10 mg Ca^{+2} per ml

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* Obtained from Scientific Service Laboratories, Inc., P. O. Box 175, Dallas, Texas 75221

disodium ethylenediamine tetraacetate [EDTA], $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$: 0.02N
sodium hydroxide, NaOH: 1N

Apparatus

burette
pH meter (or pH paper)

Procedure

1. To 100 ml of the water sample in a 250-ml Erlenmeyer flask, add a sufficient amount of 1N NaOH (<5 ml) to adjust the pH to 12-13.
2. Add 10 ml (0.1 g) 1% Cal-Red indicator and immediately titrate the solution with 0.02N EDTA. At the endpoint the color of the solution will change from wine-red to blue.
3. Repeat Steps 1 and 2 using 2.0 to 10.0 ml of standard calcium solution in 100 ml distilled water in place of the water sample.

Calculation

$$\text{calcium (mg/liter)} = \frac{1000 \times A \times B}{C \times D}$$

where A = volume of EDTA used for the sample (ml)
B = calcium in the aliquot of standard calcium solution (mg)
C = volume of water sample (ml)
D = volume of EDTA used for the standard (ml)

References

1. APHA-AWWA-WPCF. *Standard Methods for Examination of Water and Wastewater*, 12th Ed., New York, American Public Health Association, Inc. (1965)

2. Schwarzenback, G. *Complexometric Titrations*. New York, Wiley - Interscience Publishers (1957)

SECTION 6.

AIR

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SECTION 6. AIR

6.0 INTRODUCTION

The major air sampling program of the National Center for Radiological Health is the Radiation Surveillance Network [RSN] which regularly collects samples from seventy-five locations throughout the United States. The network and its analytical methods constitute an alerting system which will indicate any significant change in airborne radioactivity and provide concentration values upon which to base further action following Federal Radiation Council guides.

Analytical procedures in this Section are those used routinely by the RSN as well as those used when special studies of specific radionuclides in air are desired. Field estimates of gross beta activity in Network air samples fulfill the alerting function of the program. Laboratory measurements are made to obtain the reportable value. The laboratory measurement methods described in this Section have been used extensively and are applicable to large-scale routine operations.

The air sample, as defined by the RSN, is a filter on which particulate or adsorbable airborne material is collected continuously over a 24-hour period. Each daily sample represents about 1800 cubic meters of air drawn through the filter by a high-volume centrifugal blower. If the field estimate of the filter from any station shows 50 or more picocuries of gross beta activity per cubic meter (excluding radon daughter activity) were collected, a charcoal cartridge is inserted behind the filter. Cartridges are also used with the filters whenever the presence of airborne radioiodine is suspected.

Direct laboratory costs of the routine RSN air filter analyses for gross beta and gross gamma activity are extimated to be $2.00 per sample, including automatic data processing and recording.

6.1 PREPARATION OF SAMPLES

The air sample is obtained by drawing a large volume of air through a filter which collects most of the airborne particulates and some gases. The flow rate of air through the sampler is measured at the beginning and at the end of the sampling period.* These two values are averaged, and the average flow rate is multiplied by the operating time to determine the total volume of sampled air.

Immediately after removal from the sampler, the filter is placed in a glassine envelope. Five hours after collection, the beta-gamma activity on the filter is estimated using a portable Geiger-Mueller survey instrument, and the sample in the glassine envelope is placed in a heavy manila envelope to be mailed to the central laboratory. Charcoal cartridges are returned to their plastic bags and mailed in a heavy manila envelope.

Air filter samples need no special preparation before being counted for gross beta and gross gamma activity, and none is necessary for charcoal cartridges to be counted for gross gamma activity or analyzed by gamma spectrometry. Special preparation procedures are required only for samples which are to undergo radiochemical analysis.

6.1.1 Glass Fiber Filter

Principle of Method

A measured fraction of the filter is fused with sodium carbonate and the melt is dissolved. After destroying the silica by treatment with hydrofluoric acid, the remaining salts are dissolved and diluted to a known volume with hydrochloric acid.

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* Lockhart, L. B., Jr., R. L. Patterson, Jr., and W. L. Anderson. *Characteristics of Air Filter Media Used for Monitoring Airborne Radioactivity.* NRL Report 6054, U. S. Naval Research Laboratory (1964)

Reagents

hydrochloric acid, HCl: concentrated (12N), 6N, 2N

hydrofluoric acid, HF: concentrated (48%)

sodium carbonate, Na_2CO_3: anhydrous powder

Apparatus

platinum crucibles

muffle furnace

Procedure

1. Cut to pieces a known fractional weight of the filter, and place them in a platinum crucible.
2. Cover the sample with approximately 3 times its weight of sodium carbonate. Place in a muffle furnace and fuse at 950 ± 20° C for 30 minutes.
3. Allow the crucible to cool. Leach the melt with 50 ml distilled water, heating on a hot plate. Transfer the entire sample (solution plus solids) to a beaker.
4. Neutralize the solution with concentrated HCl; then add enough acid to make the solution 2N in HCl.
5. Filter off the silica through Whatman No. 40 filter paper. Wash twice with 2N HCl and twice with 5-ml portions of distilled water. Save the filtrate.
6. Ignite the filter paper and residue in a platinum crucible. Cool. Add 10 ml concentrated HF, and evaporate to dryness on a hot plate.
7. Add 5 ml 6N HCl and take to dryness. Repeat this step.
8. Dissolve the chloride salts remaining in the crucible with 2N HCl. Combine this solution with the filtrate from Step 5.
9. Dilute to a known volume with 2N HCl. Use this solution for analysis of plutonium, uranium, and strontium.

6.1.2 MSA* Cellulose Filter BM-2133

Principle of Method

The cellulose filter sample is ignited. The ash is treated with hydrofluoric acid to remove the silica, and the remaining chloride salts are dissolved in dilute hydrochloric acid.

Reagents

hydrochloric acid, HCl: 6N, 2N
hydrofluoric acid, HF: concentrated (48%)

Apparatus

platinum crucible
muffle furnace

Procedure

1. Place the filter sample in a platinum crucible and ignite in a muffle furnace.
2. Cool, and add 10 ml concentrated HF. Evaporate to dryness on a hot plate.
3. Add 5 ml 6N HCl and evaporate to dryness. Repeat this step.
4. Dissolve the remaining chloride salts in 2N HCl. Quantitatively transfer the solution to a volumetric flask and dilute to volume with 2N HCl.

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* Mine Safety Appliances

6.1.3 Membrane Filter

Principle of Method

The membrane filter is dissolved with acetone which is then evaporated. The residue is ignited, and the ash is treated with hydrofluoric acid to remove the silica. The remaining salts are taken up in dilute hydrochloric acid for subsequent radiochemical analysis of plutonium, uranium, and strontium.

Reagents

acetone, $(CH_3)_2CO$
hydrochloric acid, HCl: 6N, 2N
hydrofluoric acid, HF: concentrated (48%)

Apparatus

platinum crucible

Procedure

1. Place the membrane filter sample in a platinum crucible and add 5 ml acetone to dissolve the membrane. Evaporate to dryness.
2. Ignite the residue. Cool, and add 10 ml concentrated HF. Evaporate to dryness on a hot plate.
3. Follow Steps 7 through 9 of the procedure for preparing the glass fiber filter, page 6-3.

6.2 DETERMINATION OF RADIOACTIVITY

6.2.1 Gross Beta Counting

Three to five days after collection, when the sample has been received at the central laboratory and short-lived radon and thoron daughters have decayed, the filter is removed from its protective glassine envelope and placed in a 4-inch diameter stainless steel planchet. The gross beta activity is counted for one minute in a low-background, wide-area beta counting system which has been calibrated against strontium 90. A ^{90}Sr-^{90}Y performance standard is counted daily in the same system.

The sample count is recorded on a Daily Station and Laboratory Report form on which the field information has already been recorded. The count rate and activity of the standard are also recorded on this form in the appropriate spaces.

If the sample count is less than 2000 counts per minute, the sample is returned to its protective envelope and stored. If the sample count is 2000 counts per minute or greater, the sample is counted again for gross beta activity seven days later and an estimate of the age of the fission products is made using the Way-Wigner(1) decay formula.

For the lower activity level samples, the gross beta activity in picocuries per cubic meter (pCi/m^3) is computed from the count taken three to five days after collection. For the samples having higher levels of activity, age estimates are made and the beta activity is extrapolated to the time of collection using the Way-Wigner(1) decay formula.

Calculations

1. Gross Beta Activity of Air Filter Samples

The gross beta activity of the air filter samples is determined by direct comparison of the net sample count rate with that of the ^{90}Sr-^{90}Y standard. Thus,

$$\text{gross beta activity } (\text{pCi/m}^3) = \frac{A \times B}{C \times D}$$

where A = net count rate of the sample (cpm)
B = activity of the standard (pCi)
C = net count rate of the standard (cpm)
D = total volume of air collected (m^3)

2. Estimate of Fission Product Age

The estimation of fission product age is based on the Way-Wigner(1) law for decay of fission products $AT^{1.2} = K$. The equation used is:

$$D_2 = \frac{\Delta T}{1 - (A_1/A_2)^{-1/1.2}}$$

where D_2 = age in days at the time of second count
ΔT = time in days between first and second count ($T_2 - T_1$)
A_1 = activity at time of first count (pCi)
A_2 = activity at time of second count (pCi)

Table 6.2-1 is used to determine the estimated age at time of second count and to determine the activity at time of collection. For the age estimate, the ratio of activities is computed, as is the ΔT. Then, for activity ratios between 1 and 10 and ΔT values of 7 to 17 days the estimated age at time of the second count can be read from the table.

To obtain the activity at time of collection, the elapsed time in days between collection and the second count is computed.

$$\Delta T_c = T_2 - T_c$$

where ΔT_c = elapsed time from collection to second count (days)

T_2 = time of second count (days)

T_c = time of collection (days)

The estimated age D_2 as computed above is then located in the column headed by the value of ΔT_c (from 7 to 17 days) and the ratio of activities is read from the first column as the value appearing on the same horizontal line as the estimated age value. Multiplication of this ratio by the activity at the time of the second count A_2 gives the activity at time of collection A_c .

The parameters used in these calculations are illustrated in Figure 6.2-1 in relation to the Way-Wigner decay curve.

Evaluation of Data

No attempt is made to evaluate the overall accuracy of the activity measurements. A confidence level could be placed on the counting errors but this would be of questionable value since there are so many variables involved in the collection of the sample. Reproducibility of the counting results is very good, and a high confidence level could be placed on these. The gross beta activity in air for any sample should be interpreted relative to the activity in other samples measured by the same system and not as an exact value from which a specific exposure dose could be calculated.

An error term can be assigned to the estimated age since this value is dependent on counting parameters only. However, the accuracy of the age estimate is limited by the accuracy of the Way-Wigner formula in this application. The formula is based on calculations for the decay of mixed fission products from a single time of formation. Obviously, the presence of older fission products in the sample will produce a decrease in the decay rate between two counts and thus yield an age estimate greater than would be observed from fresh fission products alone. The Radiation Surveillance Network does not use the estimated age to date fresh fission product formation. It uses the estimated age only as an index to the fresh fission product content of air samples.

Table 6.2-1 Values for the Way-Wigner determination of fission product age

$\frac{A_1}{A_2}$	$\frac{D_2}{\Delta T}$	D_2 for values of ΔT (days)										
		7	8	9	10	11	12	13	14	15	16	17
1.00	∞	-	-	-	-	-	-	-	-	-	-	-
1.05	25.10	175.7	200.8	225.9	251.0	276.1	301.2	326.3	351.4	376.5	401.6	426.7
1.06	21.10	147.7	168.8	189.9	211.0	232.1	253.2	274.3	295.4	316.5	337.6	358.7
1.07	18.24	127.7	145.9	164.2	182.4	200.6	218.9	237.1	255.4	273.6	291.9	310.1
1.08	16.10	112.7	128.8	144.9	161.0	177.1	193.2	209.3	225.4	241.5	257.6	273.7
1.09	14.43	101.0	115.4	129.9	144.3	158.7	173.2	187.6	202.0	216.5	230.9	245.3
1.10	13.10	91.7	104.8	117.9	131.0	144.1	157.2	170.3	183.4	196.5	209.6	222.7
1.11	12.01	84.0	96.0	108.1	120.1	132.1	144.1	156.1	168.1	180.1	192.1	204.1
1.12	11.10	77.7	88.8	99.9	111.0	122.1	133.2	144.3	155.4	166.4	177.5	188.6
1.13	10.33	72.3	82.6	92.9	103.3	113.6	123.9	134.3	144.6	154.9	165.2	175.6
1.14	9.67	67.7	77.3	87.0	96.7	106.3	116.0	125.7	135.3	145.0	154.7	164.3
1.15	9.10	63.7	72.8	81.9	91.0	100.1	109.1	118.2	127.3	136.4	145.5	154.6
1.16	8.60	60.2	68.8	77.4	86.0	94.6	103.1	111.7	120.3	128.9	137.5	146.1
1.17	8.15	57.1	65.2	73.4	81.5	89.7	97.8	106.0	114.2	122.3	130.5	138.6
1.18	7.76	54.3	62.1	69.9	77.6	85.4	93.1	100.9	108.7	116.4	124.2	131.9
1.19	7.41	51.9	59.3	66.7	74.1	81.5	88.9	96.3	103.7	111.2	118.6	126.0
1.20	7.09	49.7	56.8	63.8	70.9	78.0	85.1	92.2	99.3	106.4	113.5	120.6
1.21	6.81	47.7	54.5	61.3	68.1	74.9	81.7	88.5	95.3	102.1	108.9	115.7
1.22	6.55	45.8	52.4	58.9	65.5	72.0	78.6	85.1	91.7	98.2	104.8	111.3
1.23	6.31	44.2	50.5	56.8	63.1	69.4	75.7	82.0	88.4	94.7	101.0	107.3
1.24	6.09	42.7	48.7	54.8	60.9	67.0	73.1	79.2	85.3	91.4	97.5	103.6
1.25	5.89	41.3	47.1	53.0	58.9	64.8	70.7	76.6	82.5	88.4	94.3	100.2
1.30	5.09	35.6	40.7	45.8	50.9	56.0	61.1	66.2	71.3	76.4	81.5	86.6
1.35	4.52	31.6	36.2	40.7	45.2	49.7	54.2	58.8	63.3	67.8	72.3	76.8
1.40	4.09	28.6	32.7	36.8	40.9	45.0	49.1	53.2	57.3	61.3	65.4	69.5
1.45	3.76	26.3	30.0	33.8	37.6	41.3	45.1	48.8	52.6	56.3	60.1	63.8
1.50	3.49	24.4	27.9	31.4	34.9	38.4	41.9	45.3	48.8	52.3	55.8	59.3

(Continued)

Table 6.2-1 Continued

$\frac{A_1}{A_2}$	$\frac{D_2}{\Delta T}$	D_2 for values of ΔT (days)										
		7	8	9	10	11	12	13	14	15	16	17
1.55	3.27	22.9	26.1	29.4	32.7	36.0	39.2	42.5	45.8	49.0	52.3	55.6
1.60	3.09	21.6	24.7	27.8	30.9	33.9	37.0	40.1	43.2	46.3	49.4	52.5
1.65	2.93	20.5	23.4	26.4	29.3	32.2	35.2	38.1	41.0	44.0	46.9	49.8
1.70	2.80	19.6	22.4	25.2	28.0	30.8	33.6	36.4	39.2	42.0	44.8	47.6
1.75	2.68	18.8	21.5	24.1	26.8	29.5	32.2	34.9	37.6	40.2	42.9	45.6
1.80	2.58	18.1	20.7	23.2	25.8	28.4	31.0	33.6	36.2	38.7	41.3	43.9
1.85	2.49	17.5	19.9	22.4	24.9	27.4	29.9	32.4	34.9	37.4	39.9	42.4
1.90	2.41	16.9	19.3	21.7	24.1	26.6	29.0	31.4	33.8	36.2	38.6	41.0
1.95	2.34	16.4	18.7	21.1	23.4	25.8	28.1	30.5	32.8	35.1	37.5	39.8
2.00	2.28	16.0	18.2	20.5	22.8	25.1	27.3	29.6	31.9	34.2	36.5	38.7
2.10	2.17	15.2	17.3	19.5	21.7	23.9	26.0	28.2	30.4	32.5	34.7	36.9
2.20	2.08	14.5	16.6	18.7	20.8	22.8	24.9	27.0	29.1	31.1	33.2	35.3
2.30	2.00	14.0	16.0	18.0	20.0	22.0	24.0	26.0	28.0	30.0	32.0	34.0
2.40	1.93	13.5	15.4	17.4	19.3	21.2	23.2	25.1	27.0	29.0	30.9	32.8
2.50	1.87	13.1	15.0	16.9	18.7	20.6	22.5	24.3	26.2	28.1	30.0	31.8
2.60	1.82	12.8	14.6	16.4	18.2	20.0	21.9	23.7	25.5	27.3	29.1	31.0
2.70	1.78	12.4	14.2	16.0	17.8	19.5	21.3	23.1	24.9	26.6	28.4	30.2
2.80	1.74	12.2	13.9	15.6	17.4	19.1	20.8	22.6	24.3	26.0	27.8	29.5
2.90	1.70	11.9	13.6	15.3	17.0	18.7	20.4	22.1	23.8	25.5	27.2	28.9
3.00	1.67	11.7	13.3	15.0	16.7	18.3	20.0	21.7	23.3	25.0	26.7	28.3
3.15	1.62	11.4	13.0	14.6	16.2	17.9	19.5	21.1	22.7	24.4	26.0	27.6
3.30	1.59	11.1	12.7	14.3	15.9	17.5	19.0	20.6	22.2	23.8	25.4	27.0
3.45	1.55	10.9	12.4	14.0	15.5	17.1	18.6	20.2	21.7	23.3	24.9	26.4
3.60	1.52	10.7	12.2	13.7	15.2	16.8	18.3	19.8	21.3	22.9	24.4	25.9
3.75	1.50	10.5	12.0	13.5	15.0	16.5	18.0	19.5	21.0	22.5	24.0	25.5
3.90	1.47	10.3	11.8	13.3	14.7	16.2	17.7	19.2	20.6	22.1	23.6	25.1
4.00	1.46	10.2	11.7	13.1	14.6	16.1	17.5	19.0	20.4	21.9	23.4	24.8

(Continued)

Table 6.2-1 Continued

$\frac{A_1}{A_2}$	$\frac{D_2}{\Delta T}$	D_2 for values of ΔT (days)										
		7	8	9	10	11	12	13	14	15	16	17
4.20	1.43	10.0	11.5	12.9	14.3	15.8	17.2	18.6	20.1	21.5	22.9	24.4
4.40	1.41	9.9	11.3	12.7	14.1	15.5	16.9	18.3	19.7	21.2	22.6	24.0
4.60	1.39	9.7	11.1	12.5	13.9	15.3	16.7	18.1	19.5	20.8	22.2	23.6
4.80	1.37	9.6	11.0	12.3	13.7	15.1	16.5	17.8	19.2	20.6	21.9	23.3
5.00	1.35	9.5	10.8	12.2	13.5	14.9	16.2	17.6	19.0	20.3	21.7	23.0
5.25	1.34	9.3	10.7	12.0	13.4	14.7	16.0	17.4	18.7	20.0	21.4	22.7
5.50	1.32	9.2	10.5	11.9	13.2	14.5	15.8	17.1	18.5	19.8	21.1	22.4
5.75	1.30	9.1	10.4	11.7	13.0	14.3	15.6	16.9	18.2	19.6	20.9	22.2
6.00	1.29	9.0	10.3	11.6	12.9	14.2	15.5	16.8	18.1	19.3	20.6	21.9
6.50	1.27	8.9	10.1	11.4	12.7	13.9	15.2	16.5	17.7	19.0	20.3	21.5
7.00	1.25	8.7	10.0	11.2	12.5	13.7	15.0	16.2	17.4	18.7	19.9	21.2
7.50	1.23	8.6	9.8	11.1	12.3	13.5	14.8	16.0	17.2	18.4	19.7	20.9
8.00	1.21	8.5	9.7	10.9	12.1	13.4	14.6	15.8	17.0	18.2	19.4	20.7
8.50	1.20	8.4	9.6	10.8	12.0	13.2	14.4	15.6	16.8	18.0	19.2	20.4
9.00	1.19	8.3	9.5	10.7	11.9	13.1	14.3	15.5	16.7	17.9	19.1	20.2
9.50	1.18	8.3	9.4	10.6	11.8	13.0	14.2	15.4	16.5	17.7	18.9	20.1
10.00	1.17	8.2	9.4	10.5	11.7	12.9	14.1	15.2	16.4	17.6	18.8	19.9

A_1 = Activity at the first counting

A_2 = Activity at the second counting

ΔT = Days between first and second counts

D_2 = Age of fission products at the time of the second count

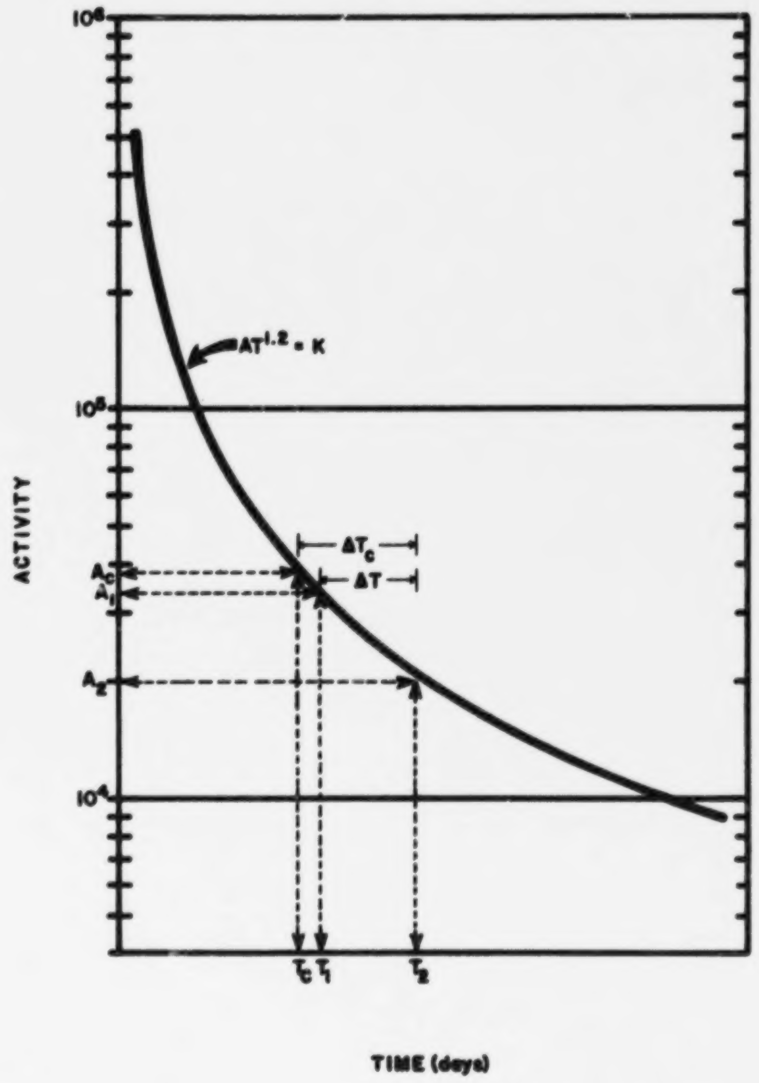

Figure 6.2-1 The Way-Wigner$^{(1)}$ decay curve

Reference

1. Way, K. and E. P. Wigner. "The rate of decay of fission products". *Phys Rev 73*:1318-1330 (1948)

6.2.2 Gamma Counting

GAMMA PULSE HEIGHT ANALYSIS

Air samples found to have more than 2000 counts per minute of gross beta activity when counted three to five days after collection are analyzed by gamma spectrometry to identify and measure the content of gamma emitters, especially fresh fission products. Charcoal cartridges are analyzed by the same method. Data from these spectral analyses provide identification of specific nuclides, particularly radioiodine, thus indicating the presence of fresh fission products.

Each sample is placed directly on a 4-inch long by 4-inch diameter thallium-activated sodium iodide [NaI(Tl)] crystal. The crystal is centered in a steel shield six inches thick having inside dimensions of 20 by 24 by 24 inches. The pulse height analyzer is set to scan 200 channels of 10 kiloelectron volts (Kev) each. Useful information is obtained from 195 channels spanning the energy range of 0.06 to 2.00 million electron volts (Mev).

The background spectrum is subtracted from the sample spectrum and the resulting net spectral data are examined, in tabular form, to locate peak areas and to tentatively identify radionuclides. Difference spectra are obtained by the Spectrum Stripping technique described in SECTION 1 and are used to estimate decay rates in peak areas and to assist in identifying short-lived nuclides (half-life of 2 to 15 days).

The Radiation Surveillance Network uses an IBM 1620 computer to resolve complex gamma spectra and to estimate the concentrations of specific gamma emitting nuclides in the sample by the peak summing method reported by Covell(1) and Burrus(2). This is essentially the method described as Compton Continuum Subtraction in 1.1.3 of SECTION 1. INSTRUMENTATION.

This method is useful in analyzing samples which have similar spectra. Such samples are apt to be collected from a given area after a particular release of radioactive material has occurred. The sample containing the highest concentration of radioactivity is counted daily in the scintillation spectrometer system for at least two weeks. Ten-minute counts are taken. All other samples having similar spectra are counted twice, the second count taken 4 or 5 days after the first. The background is subtracted from each spectrum, and the net spectra are then smoothed by averaging each three successive channels from the sixth to the fiftieth channel and each five successive channels above channel 50. The smoothed spectra are plotted on a Calcomp 565 plotter.

The smoothed spectrum of the highest sample is then resolved by the Spectrum Stripping method discussed in SECTION 1. The smoothed spectra of all other samples are then compared with this resolved spectrum, and if the spectra are similar, the quantity of the radionuclide represented by each peak is determined by direct comparison with the corresponding peak in the resolved spectrum using the picocuries to counts per minute ratios.

This procedure provides rapid and relatively accurate analysis for large numbers of samples having similar spectra. The accuracy of the method depends heavily on the quality of the standards and the preparation of the spectrum library, on the complexity of the spectra being resolved, and on the experience and judgment of the analyst. The procedure is equally applicable to gamma pulse height analysis of membrane filters, cellulose filters, and charcoal cartridges.

Calculation

The formula used in the peak summing method of estimating gamma activity of a specific peak is the following:

$$\text{activity } (\text{pCi/m}^3) = \frac{\sum_{i=x}^{i=y} A_i - \frac{N}{2}\left(A_{x-1} + A_{y+1}\right) - B}{2.2 \times C \times D \times E}$$

where activity = quantity of radionuclide at the time of count (pCi/m^3)

i = channel number

N = number of adjacent channels summed over the range $i=x$ to $i=y$

A_i = net counts recorded in channels $i=x$ to $i=y$

B = peak interference in net counts

C = counting efficiency in the summed region of i=x to i=y (cpm/dpm)

D = counting time (minutes)

E = sample volume (cubic meters of air)

2.2 = disintegrations per minute per picocurie (dpm/pCi)

References

1. Covell, D. F. "Determination of gamma-ray abundance directly from total absorption peak". *Anal Chem 31*:1785-1790 (1959)

2. Burrus, W. R. "Unscrambling scintillation spectrometer data". *IRE Trans on Nucl Sci, NS-7, 2-3*:102-111 (1960)

6.2.3 Plutonium

Plutonium nuclides in the atmosphere originate from atmospheric testing of nuclear devices and from burnup of aerospace systems which use plutonium as a power source. Information on the transfer of these radionuclides through the environment to man is useful in evaluating potential health hazards from these sources. From the mean concentration of plutonium in air the amount of plutonium ultimately reaching the blood through inhalation can be estimated. The intake of plutonium from these sources can then be compared with intake from other sources, and their potential as a future health hazard can be evaluated. Nuclear accidents can also serve as sources of plutonium contamination of the atmosphere in a local area near the accident site.

The Radiation Surveillance Network makes no attempt to measure individual plutonium isotopes but determines the "total plutonium" content of the sample.

ELECTRODEPOSITION

Plutonium in air samples of the Radiation Surveillance Network is determined by electroplating the plutonium on stainless steel from a purified solution of the sample. Alpha activity of the deposited plutonium is counted in an internal proportional alpha counter and reported as "total plutonium" although it consists primarily of plutonium 239. Any other alpha emitting plutonium isotopes present in the sample will be included, as will traces of uranium which are carried through the purification procedure. The amount of plutonium present can also be determined by alpha spectrometry. However, the energies of alpha particles from plutonium 239 and plutonium 240 are not sufficiently different to be separated by alpha spectrometry. Therefore, the activity is still reported as "total plutonium".

Principle of Method

Soluble plutonium as the chloride salt is reduced to the trivalent state and coprecipitated as the fluoride with lanthanum carrier. The fluoride precipitate is dissolved in acid aluminum nitrate solution from which plutonium is extracted into thenoyltrifluoroacetone to separate it from impurities carried with the lanthanum. Plutonium is then back extracted into strong acid, oxidized, and electrodeposited on stainless steel for counting of alpha activity.

Reagents

aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$: ∿0.45N acidity

carrier solution:

La^{+3} as lanthanum nitrate, $La(NO_3)_3 \cdot 6H_2O$: purified, 20 mg La^{+3} per ml

hydrochloric acid, HCl: concentrated (12N), 8N, 2N

hydrofluoric acid, HF: concentrated (48%), 1.5N

hydroxylamine hydrochloride, $NH_2OH \cdot HCl$: crystals

methyl orange indicator: 0.1% w/v

nitric acid, HNO_3: concentrated (16N), 8N

phenolphthalein indicator: 0.1% w/v in alcohol

potassium hydroxide, KOH: 8N, 2N

sodium hypochlorite, NaOCl: ≥5% available chlorine

sodium nitrite, $NaNO_2$: 2N

2-thenoyltrifluoroacetone [TTA]: 5.6% w/v in xylene

Apparatus

electrodeposition unit: The unit used for Radiation Surveillance Network samples was designed and fabricated by the Network's Electronics Section to accomodate six cells operated simultaneously and independently. Six current control sections plus one master voltage control unit comprise the control panel section. Each cell control section contains a coarse and vernier current adjustment. A 0-50 milliammeter is provided in each cell circuit to indicate current density. A current multiplier selector switch in each circuit provides a current range of 0-50 ma, 0-500 ma, and 0-2 amps. The line voltage of 115 AC is converted to 230V DC. The annode stirring rods are made of 0.625-inch pure platinum wire, and a speed-control switch and fuse are provided for each stirring motor.

internal proportional alpha counter

polished stainless steel planchets: 1-3/4 inch diameter, 0.032 inches thick

platinum crucibles: 250-ml and 75-ml capacity

shaker, mechanical wrist action (Burrell)

Procedure

1. Pipette an aliquot of solution prepared by one of the methods in 6.1.1 or 6.1.2 into a 100-ml polyethylene centrifuge tube, and dilute to 75 ml with 2N HCl.
2. Add 1 g $NH_2OH \cdot HCl$ crystals and 1 ml purified lanthanum carrier solution. Stir to dissolve the crystals, and let stand for 10 minutes.
3. Add 10 ml concentrated HF, stir, and let stand for 10 minutes.
4. Centrifuge for 10 minutes at 2000 rpm. Decant and discard the supernate.
5. Add 10 ml 1.5N HF to the precipitate, and mix. Centrifuge for 10 minutes, and discard the supernate.
6. Dissolve the fluoride precipitate in 30 ml 0.45N aluminum nitrate. Then add 0.25 ml 2N $NaNO_2$, and stir.
7. Transfer the solution to a 125-ml separatory funnel. Wash the centrifuge tube twice with 5-ml portions of distilled water, and add the wash to the funnel.
8. Add 10 ml TTA reagent to the separatory funnel, and shake for 20 minutes. Allow the phases to separate for 5 minutes, and draw off and discard the aqueous phase.
9. Add 20 ml distilled water to the funnel and shake for 10 minutes. Allow the phases to separate, and discard the aqueous phase.
10. Repeat Step 9 using 20 ml distilled water, and repeat again using 10 ml distilled water.
11. Add 10 ml 8N HCl to the funnel and shake for 20 minutes to extract the plutonium. Allow the phases to separate for 5 minutes and collect the acid phase in a 50-ml beaker. Repeat with 5 ml 8N HCl and combine the acid phases.
12. Evaporate the acid solution to a volume of 1-2 ml. Do not allow the sample to evaporate to dryness.
13. Neutralize the remaining solution by adding 8N KOH drop by drop in the presence of phenolphthalein indicator. Be careful not to exceed the endpoint because Pu^{+4} will precipitate from alkaline solution.

14. Add 2 ml NaOCl solution and 5 ml 2N KOH in that order. Evaporate carefully to about 5 ml.

15. Cool, and transfer the solution to a Teflon cell with enough distilled water to give a total volume of 10 ml.

16. Clamp the cell in position on the electrodeposition unit, turn on the power and adjust the voltage and current to read 7.5V and 200 ma.

17. Electroplate for at least 5 hours. Then remove the cell before turning off the current. Pour off the caustic solution, and rinse the cell thoroughly with distilled water.

18. Remove the stainless steel planchet, rinse with distilled water, and drain. Flame the planchet to cherry red over a burner. Cool, and count the alpha activity of the "weightless" sample in an internal proportional counter.

Calculation

$$\text{total plutonium activity (pCi/m}^3) = \frac{A}{B \times C \times D \times E}$$

where A = net count rate of the sample (cpm)

B = counter efficiency (cpm/pCi)

C = sample aliquot (fraction of total volume)

D = sample volume (m^3)

E = recovery of plutonium

Evaluation of Data

The plutonium recovery in these "weightless" samples is estimated to be >83% for samples containing approximately 1 to 10 picocuries of plutonium and >95% for samples containing greater amounts of plutonium. Self-absorption losses are negligible, and the technique is not influenced by gross uranium contamination.

Reference

Buluchaudra, J. "A survey of the plating processes applied to Ti, Zr, No, Be, W, Ru, and Pu". *Symposium on Electrodeposition.* Metal Finishing, Daraikudi, India (1960) p. 63

Chenley, R. B., G. J. Hunter, and T. J. Webber. "A study of the accuracy and precision of the lanthanum fluoride coprecipitation method for the determination of plutonium". AERE-C/M-327, UKAEA, Woolwich Outstation, England (1958)

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6.2.4 Uranium

Uranium isotopes are found in samples of air when atmospheric testing of nuclear devices has recently occurred. Surveillance activities to detect and measure uranium therefore serve as an indicator to the need for making necessary adjustments in sampling programs.

Total uranium in RSN samples is determined by electrodeposition on nickel-plated copper after being separated from interfering radionuclides by ion exchange. Iron, the element occurring most commonly with uranium, is adsorbed on the resin with uranium but does not interfere with the detection of uranium as it does in a fluorometric method.

ELECTRODEPOSITION

Uranium is determined in air samples prepared by the methods described in 6.1 by separating it from interfering radionuclides such as potassium 40, thorium, and radium, and then electroplating it with an efficiency of 85-95%. The alpha activity of the "weightless" sample is counted as total uranium.

Principle of Method

Soluble uranium as the chloride is adsorbed on a strongly basic ion exchange resin pretreated with 6N hydrochloric acid. Interfering ions are eluted with 9N hydrochloric acid and the uranium is then eluted with 1N acid. Although iron, which commonly occurs with uranium, is also eluted it does not interfere with the analysis. The uranium is converted to a nitrate, dissolved in dilute ammonium oxalate, and from this solution is electrodeposited on a nickel-plated copper disk. The alpha activity of the deposited sample is counted in an internal proportional counter to determine the total uranium activity.

Reagents

ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$: 0.032N ethyl alcohol, C_2H_5OH: absolute (100%)

hydrochloric acid, HCl: concentrated (12N), 9N, 6N, 1N

anion-exchange resin: Dowex 1-X4 (Cl^- form, 50-100 mesh)

nickel sulfate, $NiSO_4 \cdot 6H_2O$: 0.5M plating solution

nitric acid, HNO_3: concentrated (16N), 8N, 1N

Apparatus

electrodeposition unit: The unit used for Radiation Surveillance Network samples was designed and fabricated by the Network's Electronics Section to accomodate six cells operated simultaneously and independently. Six current control sections plus one master voltage control unit comprise the control panel section. Each cell control section contains a coarse and vernier current adjustment. A 0-50 milliammeter is provided in each cell circuit to indicate current density. A current multiplier selector switch in each circuit provides a current range of 0-50 ma, 0-500 ma, and 0-2 amps. The line voltage of 115 AC is converted to 230V DC. The annode stirring rods are made of 0.625-inch pure platinum wire, and a speed-control switch and fuse are provided for each stirring motor.

internal proportional alpha counter

ion-exchange system: A glass column 30 cm long, 1.9 cm in diameter, with a stopcock and fritted-glass disk at the bottom, filled with 30 ml of wet resin. Condition the resin by placing 500 ml of 6N HCl in a separatory funnel attached to the top of the column and letting it flow over the resin at a rate of 2 milliliters per minute (ml/min).

nickel-plated copper disk: Polish a copper disk, 1.75-inch diameter and 0.032-inch thickness, to a high luster. Place the disk in the Teflon plating cell. Add 10 ml of nickel sulphate plating solution to the cell and electroplate at a current of 150 milliamps with the platinum stirrer anode set at 200 rpm. Plate for 7 minutes and then, without turning off the current, remove the cell. Then reduce the amperage and turn off the power. Wash the disk with distilled water, dry, and polish again to a high luster.

shaker: mechanical wrist-action (Burrell)

Procedure

1. Pipette an aliquot of solution prepared by one of the methods in 6.1 PREPARATION OF SAMPLES into a 250-ml beaker and add enough concentrated HCl to make the solution 6N HCl. The final volume should be approximately 200 ml.
2. Transfer the acid solution to a separatory funnel and attach the funnel to the top of the ion-exchange column. Let the solution flow through the system at 2 ml/min. Discard the effluent.
3. Place 200 ml 9N HCl in the separatory funnel, and wash the resin at a flow rate of 2 ml/min. Discard the effluent.
4. Place 150 ml 1N HCl in the separatory funnel, and elute uranium from the resin by letting the eluant flow at a rate of 2 ml/min. Collect the eluate in a 250-ml beaker.
5. Evaporate the eluate to dryness on a hot plate. Add 5 ml 1N HNO_3 and evaporate to dryness. Repeat the evaporation with 5 ml 1N HNO_3.
6. Add two 10-ml portions and one 5-ml portion of 0.032N ammonium oxalate to the residue in the beaker, policing the beaker with each portion of ammonium oxalate and transferring the solution to a Teflon cell having a nickel-plated copper disk at the bottom.
7. Clamp the cell in position on the electrodeposition unit. Turn on the power, adjust the voltage and current at 7 volts and 40 milliamperes. Set the platinum stirrer anode at approximately 200 rpm.
8. Electroplate for at least 17 hours, preferably overnight. Remove the cell before turning off the current. Discard the electrolyte, and rinse the cell with distilled water.
9. Remove the nickel-plated disk, rinse it with water and then with absolute ethyl alcohol. Flame over a burner, cool, and count the alpha activity in an internal proportional counter.

Calculation

$$\text{total uranium activity (pCi/m}^3) = \frac{A}{B \times C \times D \times E}$$

where A = net count rate of the sample (cpm)

B = counter efficiency (cpm/pCi)

C = sample aliquot (fraction of total sample)

D = sample volume (m^3)

E = recovery of uranium

Evaluation of Data

Electroplating efficiencies have ranged consistently from 85% to 95%. The limit of detectability is about 3 pCi of uranium.

References

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6.2.5 Strontium 89 and Strontium 90

Although most of the radiostrontium burden in humans comes from ingestion rather than inhalation, measurement of radiostrontium levels in air is important to define atmosphere-to-plant and atmosphere-to-soil ratios used in predicting internal exposures. Also, much of what is known about atmospheric transport and residence times is based on strontium 90 data.

OXALATE PRECIPITATION

Principle of Method

Strontium and barium carriers are added to the acid solution of the sample. Alkaline earth carbonates are precipitated and then converted to nitrates, precipitating strontium and barium nitrate. The nitrate precipitate is dissolved in distilled water and purified by a hydroxide scavenge. Barium and radium are removed by chromate precipitation. The remaining solution is acidified, yttrium carrier is added, and the solution is stored for decay of strontium 90 to yttrium 90.

Yttrium is then separated from the strontium by precipitation as the hydroxide. The hydroxide precipitate is dissolved in hydrochloric acid and yttrium oxalate is precipitated at pH 1.5. The dried oxalate precipitate is weighed to determine the yttrium recovery and then counted for the beta activity of yttrium 90.

Strontium is precipitated as the carbonate. The dry carbonate precipitate is weighed to determine the total strontium recovery and counted for total radiostrontium beta activity. The strontium 89 activity is computed as the difference between the activity of total radiostrontium and the activity due to the strontium 90 (counted as yttrium 90).

Reagents

acetic acid, CH_3COOH: glacial (17N), 6N
ammonium acetate, $NH_4C_2H_3O_2$: 6N

ammonium hydroxide, NH_4OH: concentrated (15N), 6N

carrier solutions:

- Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
- Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20 mg Sr^{+2} per ml
- Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per ml

diethyl ether, $(C_2H_5)_2O$: anhydrous

ethyl alcohol, C_2H_5OH: absolute (100%)

hydrochloric acid, HCl: concentrated (12N), 6N

hydrogen peroxide, H_2O_2: 30% solution

nitric acid, HNO_3: fuming (90%), concentrated (16N), 8N, 1N

oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N

sodium carbonate, Na_2CO_3: crystals, 3N, 0.1N

sodium chromate, Na_2CrO_4: 0.6N

sodium hydroxide, NaOH: 10N

Apparatus

Buchner funnel, polyethylene
desiccator
drying oven
low-background beta counter
magnetic stirrer, with stirring bars
stainless steel suction-filtration apparatus (Tracerlab)

Procedure

1. Pipette into a 250-ml beaker an aliquot of the air sample dissolved by one of the methods in 6.1 PREPARATION OF SAMPLES. Add 1.0 ml each of strontium and barium carrier solutions and stir for 15 minutes using a magnetic stirrer.
2. Dilute the solution to about 200 ml with distilled water, and with continuous stirring adjust the pH to 8 with 10N NaOH.
3. Add 1.0 g sodium carbonate and continue stirring for 15 minutes. Allow the precipitate to settle for 3 hours.
4. Decant and discard the supernatant solution, and transfer the precipitate with the remaining supernate to a 90-ml centrifuge tube. Centrifuge, and discard the supernate.
5. Wash the beaker with approximately 30 ml of distilled water in several

portions, transferring the wash to the centrifuge tube containing the precipitate. Stir, centrifuge, and discard the supernate.

6. Dissolve the carbonate precipitate in 10 ml 8N HNO_3 and transfer the solution to a 250-ml beaker. Evaporate to near dryness on a hot plate. Evaporate slowly to prevent bumping.
7. Add 23 ml distilled water and 77 ml fuming HNO_3, and mix for 15 minutes using the magnetic stirrer. This solution will be 75% HNO_3.
8. Allow the nitrate precipitate to settle. Then filter with suction through a 4.25-cm diameter glass fiber filter. Allow the filter to dry, and discard the filtrate.
9. Turn off the suction. Transfer any precipitate remaining in the beaker to the funnel with a minumum volume of distilled water, and collect the solution of nitrates in a clean 250-ml beaker. If no precipitate remains in the beaker, use a small volume of distilled water to dissolve nitrates on the filter.
10. Evaporate the solution to dryness on a hot plate.
11. Repeat Steps 7-10.
12. Dissolve the residue in distilled water, transfer the solution to a 40-ml centrifuge tube, and bring the volume to 20 ml.
13. Adjust the pH to 8 with concentrated NH_4OH to check for phosphate. If no precipitate is visible, adjust the pH to 2 with 1N HNO_3; if a precipitate is present, repeat the fuming HNO_3 separation as in Steps 7-10.
14. Add 1 ml yttrium carrier solution and heat in a water bath regulated at 90° C.
15. Adjust the solution to pH 8 with concentrated NH_4OH, heat in the water bath for 5 minutes, cool to room temperature, and allow the precipitate to settle.
16. Centrifuge for 10 minutes, and transfer the supernate to a second centrifuge tube.
17. Dissolve the precipitate in a minimum volume of concentrated HCl, dilute to 15 ml with distilled water, and repeat Steps 15-16.
18. Discard the precipitate. Combine the supernatant solutions in the centrifuge tube from Step 16, and bring the total volume to 25 ml with distilled water. Add 1 ml 6N acetic acid and 2 ml 6N ammonium acetate solution. Using a pH meter, adjust the pH to 5.5 with 6N NH_4OH.

19. To precipitate barium chromate, heat the solution in a water bath and add dropwise with stirring 1 ml 0.6N Na_2CrO_4 solution. Digest in a water bath for 30 minutes, cool to room temperature, and centrifuge for 10 minutes.

20. Decant the supernate into a 2-oz polyethylene bottle. Add 1N HNO_3 to bring the pH to 2. Add 1 ml yttrium carrier solution, and store for approximately 2 weeks for yttrium 90 to grow in.
[Note: The precipitate can be analyzed for radium 226 by a radon emanation method.]

21. After a sufficient period of ingrowth, transfer the solution from Step 20 into a 40-ml centrifuge tube. Add distilled water to bring the volume to 25 ml.

22. Adjust the pH to 8 with concentrated NH_4OH. Stir, and add 3 drops of 30% H_2O_2. Heat in a water bath to hasten the precipitation of yttrium hydroxide [$Y(OH)_3$].

23. Cool to room temperature, and centrifuge for 10 minutes. Decant the supernate into a 100-ml beaker. RECORD THE TIME OF SEPARATION AS THE BEGINNING OF YTTRIUM 90 DECAY IN THE PRECIPITATE AND YTTRIUM 90 INGROWTH IN THE TOTAL STRONTIUM SUPERNATE.

24. Dissolve the precipitate by adding concentrated HCl a drop at a time, and dilute the solution to 25 ml with distilled water.

25. Repeat Steps 22-23. Combine the supernatant liquids for total radiostrontium determination.

26. Add 6N HCl to the precipitate a drop at a time until it just dissolves. Dilute with 25 ml distilled water, add 5 ml 2N oxalic acid, and using a pH meter, adjust the pH to 1.5 with 6N NH_4OH.

27. Heat in a water bath for 30 minutes to digest the precipitate. Cool to room temperature, and filter through a pre-weighed 2.4-cm diameter glass fiber filter in the suction-filtration apparatus.

28. Wash the oxalate precipitate with one 10-ml portion of distilled water, using the water to rinse the centrifuge tube. Dry the precipitate with three 10-ml portions of absolute ethyl alcohol and three 10-ml portions of diethyl ether. Continue suction for 2 minutes.

29. Weigh after a delay of 10 minutes, and calculate the recovery of yttrium carrier by dividing the weight of the yttrium oxalate precipitate [$Y_2(C_2O_4)_3 \cdot 9H_2O$] by the weight of yttrium oxalate obtained from

1 ml of yttrium carrier solution.

30. Transfer the filter and precipitate to an appropriate counting dish or planchet. Count the beta activity of yttrium 90 in a low-background beta counter. RECORD THE TIME OF COUNTING.

31. Heat the supernate from Step 25 in a water bath for 15 minutes. Then slowly add 10 ml 3N Na_2CO_3 solution with vigorous stirring. Heat in a water bath for 30 minutes.

32. Cool to room temperature, and filter with suction through a pre-weighed 2.4-cm diameter glass fiber filter. Wash the strontium carbonate precipitate with 0.1N Na_2CO_3 solution.

33. Dry in an oven at 110° C for 20 minutes and cool in a desiccator for 10 minutes. Weigh, and calculate the recovery of strontium carrier as strontium carbonate.

34. Transfer the filter and precipitate to an appropriate counting dish. Count the radiostrontium beta activity in a low-background beta counter. RECORD THE TIME OF COUNTING.

Calculations

$$\text{strontium 90 activity (pCi/m}^3\text{)} = \frac{A}{B \times C \times D \times E \times F \times G \times H}$$

where A = net count rate of yttrium 90 (cpm)

B = total air sample volume (m^3)

C = fraction of total volume analyzed

D = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a glass fiber filter (cpm/pCi)

E = chemical recovery of yttrium [from Step 29]

F = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from separation of yttrium [Step 23] to the time of counting [Step 30]

G = strontium carrier recovery

H = correction factor $1-e^{-\lambda t}$ for yttrium ingrowth where t is the time from the first separation of yttrium from strontium to the separation following the storage period

$$\text{strontium 89 activity (pCi/m}^3\text{)} = \frac{1}{B \times C}\left[\frac{A}{D \times E \times F} - G(H + I \times J)\right]$$

where A = net beta count rate of total radiostrontium (cpm)

B = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from sample collection to the time of counting

C = counting efficiency for counting strontium 89 as strontium carbonate mounted on a glass fiber filter (cpm/pCi)

D = strontium carrier recovery [from Step 33]

E = total air sample volume (m^3)

F = fraction of total volume analyzed

G = strontium 90 activity as computed from the yttrium 90 activity (pCi/m^3)

H = counter efficiency for counting strontium 90 as strontium carbonate mounted on a glass fiber filter (cpm/pCi)

I = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a glass fiber filter (cpm/pCi)

J = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from separation of the strontium [Step 23] to the time of counting [Step 34]

References

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6.2.6 Radioiodine

Radioiodine in air filter and cartridge samples can usually be identified and quantitated by gamma pulse height analysis if the spectrometer detector system is properly calibrated (see 1.1.3 and 1.1.4). If iodine 132 is present in the mixture, it will be in equilibrium with its tellurium 132 parent. The 0.23 Mev peak of tellurium 132 can be quantitated using one of the methods discussed in SECTION 1. INSTRUMENTATION and the amount of iodine 132 can be computed from its equilibrium ratio.

Analysis of iodine 131 often ignores the fact that bismuth 214, a radon daughter, has a peak in the 0.36 Mev region. Since the half-life of radon is 3.85 days, one cannot store the sample for radon decay before counting. Carbon tetrachloride extraction of iodine from the air filter samples effectively eliminates bismuth 214 interference. Unfortunately, quantitative removal of iodine from charcoal is not readily obtained.

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SECTION 7.

OTHER ENVIRONMENTAL SAMPLES

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SECTION 7. OTHER ENVIRONMENTAL SAMPLES

7.0 INTRODUCTION

This Section describes the preparation and analysis of environmental samples other than those covered in Sections 3 through 6. Procedures included here are normally performed in the National Center's radiological health laboratories by chemists and experienced technicians. They are not easily adapted to routine "mass-production" operation, since more or less constant attention of the analyst is required for individual samples, especially during wet-ashing procedures.

Three general techniques for putting samples into a soluble form prior to analysis are described under 7.1 SAMPLE PREPARATION. Dry ashing is least demanding of the analyst's attention, but it cannot be used to prepare samples for analysis of materials which volatilize at dry-ashing temperatures. Acid digestion, or wet ashing, requires almost constant attention of the analyst and, assuming the necessary equipment is available, at least one day is required to prepare up to four samples by this technique. Fusion must be used for soil and silt and other samples having a high silica content.

After the samples are put into solution, they can be analyzed for radionuclides by the procedures given in 7.2 DETERMINATION OF RADIOACTIVITY. The nuclide to be analyzed determines to some extent the preparation technique required. Thus, polonium 210 cannot be determined in a sample which has been prepared by dry ashing.

Procedures for determining stable elements routinely associated with the radiochemical methods are very similar or identical to those used for sample types discussed in other Sections. They vary mainly in preliminary steps for converting the sample into a form which can be analyzed. Thus, procedures for determination of stable elements are given in part 7.3 by reference to methods in other Sections.

7.1 PREPARATION OF SAMPLES

Little pretreatment is required for samples prepared by procedures given in this Section. Bone (especially human bone) and soft tissue samples should be preserved with paraformaldehyde and stored in a freezer prior to use. Urine samples should be kept in 10% hydrochloric acid to prevent any decomposition. Soil and silt samples require no special pretreatment unless they are biologically contaminated. All normal biological laboratory safety regulations must be observed when handling biological or pathological samples.

7.1.1 Dry Ashing

Dry ashing is used to prepare organic samples for analysis of nonvolatile radionuclides. Samples to be analyzed for iodine, polonium, or other nuclides which are volatile at temperatures below 500° to 800° C should not be prepared this way.

Because of their high organic content, soft tissue samples tend to swell or spatter as they are ashed, even after being dried. The resulting loss of sample can be minimized by increasing the furnace temperature gradually and in small increments, by dissecting or homogenizing the sample, and by using a crucible large enough to contain spatters or swelling.

VEGETATION

By this procedure vegetation, including tobacco, kale, etc., is prepared for analysis of nonvolatile radionuclides such as lead 210, bismuth 210, and radium 226.

Principle of Method

The samples are dried at 105° C. They are then ashed in a muffle furnace at 550° C, and the ash is dissolved in hydrochloric acid.

Reagents

hydrochloric acid, HCl: concentrated (12N), 6N

Apparatus

No special apparatus is required.

Procedure

1. Place 500 grams of sample in a Coors type evaporating dish and dry in an oven at 105° C for 24 hours.
2. Transfer the dish to a muffle furnace. Slowly bring the temperature up to 550° C, and hold at that temperature for five hours.
3. Remove the dish from the furnace and allow it to cool. Add 75 ml of 6N HCl, and digest on a hot plate. Centrifuge the digest, and filter the supernate through a glass fiber filter, using suction. Retain the filter for use in Step 4.
4. Slurry the residue in the centrifuge tube with 30 ml of concentrated HCl, and digest on a hot plate for several hours. Filter the digest through the same filter used in Step 3. Wash the residue thoroughly with distilled water.
5. Combine the filtrates from Steps 3 and 4, and dilute to a known volume. The sample is now ready for radiochemical analysis.

BONE

Dry ashing is used to prepare bone samples for analysis of nonvolatile radionuclides. Although cesium 137 is volatile at the final ashing temperature, it can be analyzed by gamma spectrometry after the first ashing stage is completed. Bone samples from any source may be used as long as any extraneous tissue is first removed. The time required for complete preparation is usually two to three days, and the number of samples which can be processed at one time depends on the capacity of the equipment available.

Principle of Method

The sample is ashed in two stages, first at 450° C, and finally, after grinding, at 800° C.

Reagents

None

Apparatus

alundum (or platinum) crucibles
Pyroceram* dishes

Procedure

1. Weigh the bone sample in a Pyroceram* dish, and place it in a muffle furnace. Bring the temperature to 450° C and hold for 16 to 24 hours.
2. Remove the sample from the furnace, cool, and reweigh.
3. Grind the sample with a mortar and pestle, and place the pulverized ash in an alundum crucible.
   [Note: If a cesium 137 determination is required, a measured amount of this ash is transferred to a 1-pint plastic container similar to a cottage cheese container and analyzed by gamma spectrometry. (See SECTION 1, 1.1.3 and 1.1.4.) After scanning, proceed with Step 4.]
4. Place the sample in a muffle furnace, and bring the temperature to 800° C. Hold at that temperature for 16 to 24 hours.

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* Corning Ware - registered trademark

5. Remove the sample from the furnace, allow it to cool, and weigh the ash. If desired, the sample can be stored as the ash prior to radiochemical analysis.

BLOOD PLASMA

This procedure is used to prepare blood plasma (or serum) for analysis of nonvolatile radionuclides such as lead 210, radium 226, and strontium 90. All blood cells should be removed from samples submitted as whole blood before this procedure is applied.

Principle of Method

The blood plasma is dried at 105° C. It is then ashed, first at 300° C to destroy any dextrose present, and finally at 475° C to destroy the remaining organic material.

Reagents

None

Apparatus

Pyrex dishes

Procedure

1. When whole blood is used, allow the cells to settle, and then aspirate the plasma. Place 2 liters of plasma in a large Pyrex dish, and dry in an oven at 105° C for about 48 hours.
2. Transfer the sample to a large oven, and slowly increase the temperature to 300° C. Maintain this temperature for 4 hours.
   [Note: The sample swells considerably during this phase of ashing, due to the presence of dextrose. Therefore, a large gas oven or muffle furnace must be used.]
3. Transfer the charred plasma to a Coors crucible, and place in a muffle furnace. Raise the temperature to 475° C and maintain this temperature for at least 48 hours.
4. Remove the sample from the furnace, cool, and weigh. The ash is now ready for radiochemical analysis.

HAIR

This procedure is used to prepare very large samples (up to two kilograms) of human hair for analysis of nonvolatile radionuclides such as radium 226, lead 210 and strontium 90. Smaller samples would be apt to contain less debris and could be thoroughly cleaned in fewer steps.

Principle of Method

The sample is washed thoroughly in detergent solution, to remove dirt and other foreign matter. After being dried at 105° C, the clean hair sample is placed in an electric oven and slowly ignited. Final ashing is completed in a muffle furnace at 600° C.

Reagent

detergent

Apparatus

colander
Pyroceram* or Pyrex dishes
shaker, horizontal action
wire basket

Procedure

1. Use a sample of about 1000 grams, and divide it in two or three parts. Put each part in a large pan approximately six inches deep. Fill the pan with tap water to about two inches from the top, and add detergent.
2. Place the pan on a horizontal-action shaker, and shake moderately (so that the water does not spill over the side of the pan) for about 20 minutes.

   [Note: It may be necessary to break the hair apart with your hands and remove large items such as end papers, bobby pins, cigarette butts, and other trash. Such debris is apt to be present in samples collected from beauty parlors and barbershops.]

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* Corning Ware - registered trademark

3. After shaking, carefully lift the hair off the water, allowing any of the dirt which has settled to stay at the bottom of the pan.
4. Place the hair, a small handful at a time, in a colander, and rinse it well with tap water. Examine the rinsed hair carefully, and remove any observable foreign matter which may remain.
5. Place the hair in a clean pan, and again shake with warm water and detergent for about 30 minutes. Then rinse the hair thoroughly with water.
6. Repeat Step 5.
7. Remove the pan from the shaker, reach under the hair and scoop it off the surface of the water, and place it in a colander. Try to leave as much dirt as possible on the bottom of the pan.
8. Rinse the hair thoroughly with distilled water. Shake the colander well to remove all excess water.
9. Transfer the hair to a wire basket lined with fiberglass mesh or aluminum foil. Place in a drying oven at 110° C for 48 hours.
10. Weigh the clean dry hair, and record this weight as the original sample weight.
11. Transfer the hair to a 4-quart Pyroceram or Pyrex pan, and place in an electric oven. Raise the temperature slowly to 300° C.
    [Note: Keep the temperature constant at any temperature at which smoking is heavy until the smoking stops. This first occurs at 270° C.]
12. Transfer the sample to one or more No. 6 Coors dishes, and place in a muffle furnace. Raise the temperature quickly to 600° C, and maintain this temperature for 48 hours.
    [Note: When ashing is complete, the ash is a very light tan to white color, and is very light and fluffy.]
13. When the ash has been cooled and weighed, it is ready for radiochemical analysis.

7.1.2 Wet Ashing

Samples which are volatile at dry-ashing temperatures (500° to 800° C) can be put into solution by acid digestion. The procedures for wet ashing have been used in the Center's laboratories primarily for samples requiring polonium 210 analysis. However, once the sample is in solution, it can be used for other analyses as well.

As with most biological samples, soft tissues must be preserved in paraformaldehyde and stored in a freezer prior to use. All normal laboratory safety precautions must be taken when handling biological samples, especially if the samples may contain pathogens.

TOBACCO

This procedure has been used primarily to prepare tobacco from cigarettes for analysis of polonium 210. It can be used to prepare any tobacco sample for analysis of volatile radionuclides. The method usually requires four to eight hours to complete.

Principle of Method

The sample is digested with nitric acid. Silica is removed from the digest by treatment with hydrofluoric acid, and the remaining organic material is destroyed using perchloric acid.

Reagents

hydrofluoric acid, HF: concentrated (48%)
nitric acid, HNO_3: fuming (90%), concentrated (16$\underline{N}$)
perchloric acid, $HClO_4$: concentrated (12$\underline{N}$)

Apparatus

perchloric acid hood
platinum evaporating dish
safety glasses

Procedure

1. Place the tobacco from 20 cigarettes (or an equivalent amount of tobacco from another source) in a 1-liter beaker, and moisten the tobacco with distilled water. With stirring, slowly add 600 ml of concentrated nitric acid.
2. Slowly heat the mixture on a hot plate until it boils gently. Continue boiling until the acid evaporates to a volume of approximately 100 to 150 ml.
3. Add 400 ml fuming nitric acid. Slowly heat to boiling, and evaporate to a volume of 100 to 150 ml.
4. Using distilled water, transfer the solution and the precipitate (silica) to a 250-ml centrifuge bottle. Centrifuge until the supernatant liquid is clear (usually 10-15 minutes), and decant into a 600-ml beaker.
5. Transfer the residue to a platinum evaporating dish with distilled water. Add 20 ml of concentrated HF to the platinum dish, and slowly evaporate to dryness.
6. Add an additional 30 ml of concentrated HF to the cooled residue, and again evaporate to dryness, as in Step 5. Repeat until no more silica can be removed.
7. Add to the residue 10 ml of distilled water and 10 ml concentrated HNO_3, and boil for 10 minutes. Allow the mixture to cool, and combine it with the supernate from Step 4.
8. Working in a perchloric acid hood, cautiously add 20 ml concentrated $HClO_4$ and slowly evaporate the solution until copious fumes of perchloric acid are evolved. Do not evaporate to dryness!
9. Continue fuming until the color of the solution changes from amber to light yellow-green. Violent frothing, even an explosion, may occur while evaporating nitric-perchloric acid – organic mixtures. Wear safety glasses and work behind a safety glass shield at all times. If such frothing occurs, or if the solution suddenly turns very dark, remove the sample from the hot plate and quickly leave the area. When the sample has cooled, add 10 ml concentrated HNO_3 and continue fuming.
10. When the solution appears clear, the sample is ready for radiochemical analysis.

URINE

Urine samples are prepared for radiochemical analysis by this procedure. The method is particularly applicable to bioassay procedures, and has been applied in the National Center's radiological health laboratories to prepare urine samples for determination of polonium 210.

Principle of Method

The sample is evaporated to dryness. The organic matter is destroyed by treatment with hydrogen peroxide and nitric acid. The residual salts are dissolved in dilute hydrochloric acid prior to analysis.

Reagents

hydrochloric acid, HCl: 0.5N
hydrogen peroxide, H_2O_2: 30% solution
nitric acid, HNO_3: concentrated (16N)

Apparatus

No special apparatus is required.

Procedure

1. Add 1000 ml of urine to a 2-liter beaker, and slowly evaporate to dryness on a hot plate. Work in a hood.
2. Slowly add 500 ml of concentrated HNO_3 and evaporate to dryness. [Note: If the sample is evaporated too fast, the salts are apt to ignite as the volume is reduced.]
3. Add enough concentrated HNO_3 to dissolve the salts. [The solution is usually a light straw color.] Then add 1-2 ml 30% hydrogen peroxide, and again evaporate to dryness.
4. Dissolve the salts in concentrated HNO_3 and repeat Step 3 until no more nitrous oxide [N_2O] fumes are evolved with the addition of peroxide.
5. On a hot plate, evaporate the solution to dryness and bake at a termperature below 200° C for 1 to 2 hours.
6. Dissolve the salts in distilled water, and again evaporate to dryness. If the solution is evaporated very slowly as it nears dryness, the resultant salts will be whiter.

7. Repeat Step 6 three times.
8. Add to the residue 100 ml of 0.5$\underline{N}$ HCl, and heat gently to dissolve the salts.
9. When cooled, the solution is ready for radiochemical analysis.

SOFT TISSUE

This wet-ashing procedure is used to prepare soft tissue samples (e.g., lung, liver, kidney, muscle, etc.) for radiochemical analysis of elements which are volatile at temperatures above 200° C. Its primary use in laboratories of the National Center for Radiological Health has been to prepare samples for determination of polonium 210.

Principle of Method

The sample is preserved prior to analysis by storing in a freezer. It is then defrosted, dissected if necessary, and dried at 105° C. The organic material is completely destroyed by a series of nitric-perchloric acid digestions, and silica is volatilized by hydrofluoric acid treatment. The remaining salts are dissolved in hydrochloric acid prior to analysis.

Reagents

hydrochloric acid, HCl: concentrated (12N)
hydrofluoric acid, HF: concentrated (48%)
nitric acid, HNO_3: fuming (90%), concentrated (16N)
perchloric acid, $HClO_4$: concentrated (12N)

Apparatus

perchloric acid hood
Teflon beaker, 250-ml capacity

Procedure

1. Defrost the sample, which has been stored in a freezer, by allowing it to stand at room temperature overnight.
2. Dissect the fat from organs, puncture any surface membranes which could retain gas and vapors built up during heating and thus explode, and cut into convenient-sized pieces. When working with lungs, dissect the bronchi to the second bifurcation from the main part of the lung. Dissect away the lymph nodes which are located at the entrance of the bronchi to the lung. Cut the lobes into small pieces.
3. Place each part of the sample into a pre-weighed Coors evaporating dish, and dry in an oven at 105° C for 24 hours. Reweigh the sample

in its container to determine the dry weight of the sample.

4. Transfer the sample to a 600- to 1000-ml beaker, and slowly and cautiously add concentrated HNO_3.
   [Note: When digesting lung tissue, slowly add portions of the sample to the acid, rather than the acid to the sample.]
   The sample must be watched constantly, as frothing, foaming, and spattering can occur. Heat gently to boiling on a hot plate until the sample is dissolved, and then evaporate the solution to a small volume.
5. Add fuming nitric acid to the sample, and again evaporate to a small volume. [The solution will appear dark brown when the acid is first added, due to the presence of organic material.]
6. Repeat Step 5 until the solution is light brown in color.
7. Transfer the sample to a 250-ml Teflon beaker, and add 100 ml of concentrated HNO_3 and 20 ml of concentrated $HClO_4$. Using a perchloric acid hood, evaporate the solution to the white fumes of $HClO_4$.
8. Add 50 ml of concentrated HNO_3 and again evaporate to fumes of $HClO_4$.
9. Repeat Step 8, adding concentrated $HClO_4$ as needed, until the sample is a light straw color. Then continue to fume the sample until the $HClO_4$ has been reduced to as small a volume as possible without the formation of perchlorate salts.
10. Cool the sample, and wash down the sides of the beaker with distilled water. If silica is present, continue with Step 11; if not, proceed with Step 13.
11. Add 10 ml of concentrated HF, and evaporate the solution to fumes of $HClO_4$.
12. Repeat Step 11 until all the silica is removed.
13. Wash the sides of the beaker with small amounts of concentrated HCl, and evaporate to fumes of $HClO_4$.
14. Repeat Step 13 three times.
15. Dissolve the salts in distilled water, adding several milliliters of concentrated HCl if solution is difficult. When dissolved, the sample is ready for radiochemical analysis.

7.1.3 Fusion

The fusion technique is used to prepare samples not readily dissolved by acid digestion or other techniques. Because of their high silica content, soil and silt samples must be put into solution through fusion. Ash from samples of food and biota may also be fused prior to radiochemical analysis. Almost any ashed sample not readily soluble in acid will dissolved easily after fusion.

SOIL AND SILT

This method is applicable to most soil samples and silts from river, harbor, or bay areas. The procedure requires little experience, and a technician can easily handle eight to sixteen samples per day, depending upon the amount of equipment available and the size of the samples.

Principle of Method

Sodium carbonate and sodium hydroxide are added to an aliquot of the silt or soil sample with the carriers appropriate to the radiochemical analyses to be made. The mixture is fused, and the cooled fusion mixture is dissolved in dilute hydrochloric acid.

Reagents

carrier solutions: (see reagent lists of appropriate radiochemical procedures)
sodium carbonate, Na_2CO_3: anhydrous granules or powder
sodium hydroxide, NaOH: pellets

Apparatus

nickel crucible, 250-ml capacity
nickel spatula

Procedure

1. Weigh a portion of dry silt or soil into a 250-ml nickel crucible. One to ten grams should be taken, depending upon the silica content.

Record the weight of sample.

2. Add the appropriate carrier solutions to the sample, and mix thoroughly with a nickel spatula.
3. To this mixture add 5 grams of NaOH pellets per gram of sample. Mix thoroughly.
4. Fuse over a Meeker burner for 20-30 minutes, and then slowly stir in 0.5 grams of anhydrous Na_2CO_3 per gram of soil or silt. Continue heating for 20-30 minutes.
5. Remove the crucible from the flame with long-handled tongs, and allow the melt to cool.
6. Take up the cooled fusion mixture in about 200 ml of hot distilled water. Disintegrate by gentle boiling.
7. Using distilled water, transfer the sample quantitatively to a 250-ml centrifuge bottle. Centrifuge for 5 minutes. Discard the supernate.
8. Add 40 ml of 3N Na_2CO_3. Heat for 10 minutes. Centrifuge, and discard the supernate.
9. Dissolve the precipitate in a minimum volume of 6N HCl.
10. Using distilled water, quantitatively transfer the solution to a 250-ml volumetric flask and dilute to volume. The sample is now ready for radiochemical analysis.

Reference

Porter, C. R., R. J. Augustine, J. M. Matusek, Jr., and M. W. Carter. *Procedures for Determination of Stable Elements and Radionuclides in Environmental Samples.* Public Health Service Publication No. 999-RH-10, Environmental Health Series, Radiological Health (1965)

7.2 DETERMINATION OF RADIOACTIVITY

7.2.1 Strontium 90

YTTRIUM OXALATE PRECIPITATION - Bone Ash

This method is used to analyze bone ash for strontium 90. It is faster than the TBP EXTRACTION METHOD described in 7.2.2, and is quite satisfactory for bone which has not been contaminated with other rare earth elements.

Principle of Method

Yttrium carrier is added to an aliquot of dissolved bone ash, and yttrium oxalate is precipitated from the solution at pH 1.0. The precipitate is ignited, dissolved in nitric acid, and the yttrium is separated from calcium by successive hydroxide precipitations. The yttrium is extracted into thenoyltrifluoroacetone from a pH 5 solution, and back extracted with dilute nitric acid. From the dilute acid solution, yttrium is precipitated as the oxalate which is weighed to determine the chemical yield, and then counted for the beta activity of yttrium 90.

Reagents

ammonium acetate buffer: pH 5.0
ammonium hydroxide, NH_4OH: concentrated (15N)
carrier solution:
  Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 20 mg Y^{+3} per ml
ethyl alcohol, C_2H_5OH: absolute (100%)
hydrochloric acid, HCl: concentrated (12N), 6N
nitric acid, HNO_3: 3N, 0.1N
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N
sodium carbonate, Na_2CO_3: 3N
2-thenoyltrifluoroacetone [TTA]: 10% in benzene w/v

Apparatus

desiccator

low-background beta counter

mechanical shaker (desirable, but not essential)

platinum crucible, 60-ml capacity

stainless steel suction-filtration apparatus (Tracerlab)

Procedure

1. Dissolve 10-20 grams of bone ash obtained by the procedure for ashing bone samples given in 7.1.1 Dry Ashing in 6N HCl, and dilute to 500 ml with distilled water.
2. Transfer a 200-ml aliquot of dissolved bone ash to a 400-ml beaker, and add 2.0 ml of yttrium carrier solution. Adjust the pH to 1.0 with concentrated NH_4OH, using a pH meter. Then add 80 ml of 2N oxalic acid.
3. Filter through Whatman No. 42 paper, 9.0-cm diameter, using a Buchner funnel. Discard the filtrate. Record the time of separation as the beginning of yttrium 90 decay. Transfer the precipitate and paper to a 60-ml platinum crucible, and ignite over a Meeker burner for one hour.
4. Transfer the yttrium oxide residue to a 250-ml beaker, and dissolve it in 100 ml of 3N HNO_3. Wash the crucible with 3N HNO_3, and add the wash to the beaker. Adjust the pH of the combined solutions to 1.0 with concentrated NH_4OH, and add 80 ml of 2N oxalic acid.
5. Repeat Step 3.
6. Transfer the oxalate precipitate to a 250-ml beaker, and dissolve it in 100 ml of 3N HNO_3. Wash the crucible with 3N HNO_3, and add the wash to the beaker. Heat the solution on a hot plate, and make it alkaline by adding concentrated NH_4OH. With distilled water, transfer the alkaline solution to a 250-ml centrifuge bottle. Centrifuge, and discard the supernate.
7. Dissolve the hydroxide precipitate in concentrated HCl. Dilute to approximately 100 ml with distilled water, and make the solution alkaline with concentrated NH_4OH, as in Step 6. Centrifuge, and discard the supernate.
8. Repeat Step 7 until no precipitate is formed upon the addition of Na_2CO_3 to the supernate. [This usually requires from three to five precipitations.]
9. Dissolve the final precipitate in concentrated HCl, and adjust the pH to 5 with ammonium acetate buffer.

[Note: The buffer will adjust the solution to pH 5 because much of the HCl is neutralized in dissolving the carbonate precipitate.] Transfer the solution to a 125-ml separatory funnel, using a minimum volume of distilled water. Add to the funnel 20 ml of 10% TTA in benzene, and shake for five minutes using a mechanical shaker, if available.

10. When the phases have separated, drain the aqueous phase to a clean 125-ml separatory funnel, and add 20 ml of 10% TTA in benzene. Save the organic phase. Shake the aqueous phase with the benzene for five minutes. Let the phases separate, and drain off and discard the aqueous phase.
11. Combine the organic phases from Steps 9 and 10 in one of the separatory funnels. Wash the empty funnel with 20 ml of ammonium acetate buffer, and add the wash to the funnel containing the organic material. Shake for two minutes. Let the phases separate, and drain off and discard the aqueous phase.
12. Add 10 ml of 0.1N HNO_3 to the separatory funnel, and shake for five minutes. Transfer the aqueous phase to a 40-ml centrifuge tube.
13. Repeat Step 12 twice, combining the aqueous phases in the centrifuge tube.
14. Heat the solution in a water bath. Add to it 10 ml of 2N oxalic acid and, using a pH meter, adjust the pH to 1.0-1.5 with concentrated NH_4OH. Centrifuge, and discard the supernate.
15. Add warm distilled water to the oxalate precipitate to the 40-ml mark. Stir to mix well. Then centrifuge, and discard the supernate.
16. Place a 2.4-cm diameter glass fiber filter on a stainless steel planchet and weigh them together. Place the filter onto the filtration apparatus.
17. Take up the precipitate in 10 ml warm distilled water and transfer it to the filter paper, using warm water to complete the transfer. Wash the precipitate with three 10-ml portions of absolute ethyl alcohol.
18. Carefully place the filter with the precipitate back onto the stainless steel planchet, and dry in an oven at 125° C for 20 minutes. Cool in a desiccator and reweigh together the planchet, the yttrium oxalate precipitate, and the filter. Calculate the chemical yield of yttrium by dividing the weight of the precipitate by the weight of

yttrium oxalate $[Y_2(C_2O_4)_3]$ which should be obtained from 2 ml of the carrier solution.

19. Transfer the filter to an appropriate planchet, and count for the beta activity of yttrium 90 in a low-background beta counter. RECORD THE DATE AND TIME OF COUNTING.
20. Count again after two weeks to check the purity of yttrium 90. Subtract any residual activity from the original count rate.

Calculation

$$\text{strontium 90 activity (pCi/gram of ash)} = \frac{A \times B}{C \times D \times E \times F \times G}$$

where A = net beta count rate of yttrium 90 (cpm)

B = sample volume (liters)

C = counter efficiency for counting yttrium 90 as yttrium oxide mounted on a glass fiber filter (cpm/pCi)

D = recovery of yttrium carrier

E = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from separation of yttrium [Step 10] to the time of counting

F = sample aliquot (liters)

G = weight of ash (grams)

Reference

Volchok, H. L., J. E. Gaetjen, J. L. Kulp, and W. R. Eckelmann. "Determination of ^{90}Sr and ^{140}Ba in bone, dairy products, vegetation, and soil". *Ann N Y Acad Sci 71*:293-304 (1957)

7.2.2 Strontium 89 and Strontium 90

TTA EXTRACTION PROCEDURE

By this procedure, ash from samples of food and biological materials other than bone may be analyzed for strontium 89 and strontium 90. The method has been used for routine determination of these radionuclides in ashed samples of food, hair, blood, and human organs.

Laboratory facilities needed to carry out the procedure are modest. A duplicate analysis of one sample can be performed in twenty hours, and an experienced technician can analyze six to eight samples in a five-day week.

Principle of Method

Strontium carrier is added to an aliquot of dissolved ash, and the alkaline earth carbonates are precipitated. This precipitate is dissolved in nitric acid, and silica is removed. Strontium is then precipitated as the nitrate and purified by washing with nitric acid. Any remaining phosphate is removed by conversion of alkaline earth phosphates to carbonates. Barium and radium are removed by chromate precipitation, and final purification is made by hydroxide scavenging. From the purified solution, strontium carbonate is precipitated. The precipitate is dissolved in nitric acid, yttrium carrier is added, and the solution is stored for yttrium 90 to grow in.

After an ingrowth period of at least five days, the yttrium is separated from the strontium by extraction into thenoyltrifluoroacetone from a pH 5 solution. It is back-extracted into dilute nitric acid, and precipitated as the oxalate. After being weighed to determine chemical yield, the yttrium oxalate is counted for the beta activity of yttrium 90. In a similar manner, strontium is precipitated as the carbonate which is weighed and counted for the beta activity of total radiostrontium.

Strontium 89 activity is computed as the difference between total radiostrontium and strontium 90 (as yttrium 90) activities.

Reagents

ammonium acetate buffer: pH 5.0
ammonium hydroxide, NH_4OH: concentrated (15N), 6N
carrier solutions:
  Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
  Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 90 mg Sr^{+2} per ml
  Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 20 mg Y^{+3} per ml
ethyl alcohol, C_2H_5OH: absolute (100%)
hydrochloric acid, HCl: 6N
methyl orange indicator: 0.1% w/v
nitric acid, HNO_3: concentrated (16N), 1N, 0.1N
oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N
phenolphthalein indicator, $C_{20}H_{14}O_4$: 1% w/v in alcohol
scavenger solution: 10 mg each of Fe^{+3}, Ce^{+3} and Zr^{+4} per ml
  Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$
  Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$
  Zr^{+4} as zirconium nitrate, $Zr(NO_3)_4 \cdot 5H_2O$
sodium carbonate, Na_2CO_3: 3N
sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$: 0.5N
2-thenoyltrifluoroacetone [TTA]: 10% w/v in benzene

Apparatus

desiccator
low-background beta counter
mechanical shaker (desirable, but not essential)
stainless steel suction-filtration apparatus (Tracerlab)

Procedure

1. Measure a 250-ml aliquot of dissolved ash into a 600-ml beaker. Add 1.0 ml of the strontium carrier solution.
2. Add concentrated NH_4OH until a precipitate first appears. Heat to near boiling, and slowly add 3N Na_2CO_3 until the effervescence ceases. Then add an additional 150 ml of 3N Na_2CO_3. Allow the precipitate to settle, preferably overnight. Decant or aspirate the supernatant solution, and discard it.
3. Using distilled water, quantitatively transfer the precipitate to a

250-ml centrifuge bottle. Centrifuge the sample, and discard the supernate. Wash the precipitate with distilled water. Centrifuge again, and discard the supernate.

4. Dissolve the precipitate in a few milliliters of concentrated HNO_3. Using a minimum volume of distilled water, transfer the solution to a 250-ml beaker, and take it to dryness on a hot plate.
5. Bake the residue for 20-30 minutes. Then cool and dampen the salts with a few milliliters of concentrated HNO_3. Add 50 ml of hot distilled water, and boil for several minutes. [Do not let it spatter.]
6. Filter the hot solution through Whatman No. 541 filter paper into a 250-ml beaker. Wash the empty beaker and the filter paper with warm distilled water, adding the wash to the solution. Take the solution to near dryness on a hot plate, add 10 ml of concentrated HNO_3, and again take the solution to near dryness.
7. Slurry the residual salts with concentrated HNO_3 and transfer the slurry to a 40-ml centrifuge tube with concentrated HNO_3. Heat in a water bath; then cool in an ice bath. Centrifuge, and discard the supernatant solution.
8. Fill the centrifuge tube to the 40-ml mark with concentrated HNO_3. Mix well. Heat the mixture in a water bath; then cool in an ice bath. Centrifuge, and discard the supernatant solution.
9. Dissolve the precipitate in 15 ml of distilled water. With $6\underline{N}$ NH_4OH, adjust the pH of this solution to a phenolphthalein endpoint (pH 9). Heat in a water bath, as in Step 8. Then cool, centrifuge, and transfer the supernatant solution to a 40-ml centrifuge tube.
10. To the precipitate, add 10 ml of distilled water and 10 ml of $3\underline{N}$ Na_2CO_3. Heat in a water bath for 30 minutes stirring occasionally. Centrifuge the mixture and discard the supernatant solution. Dissolve the precipitate in 2 ml of concentrated HCl, and combine this solution with the supernate from Step 9. Discard any insoluble residue.
11. Adjust the pH of the solution to a methyl orange endpoint (pH 4.5) with $6\underline{N}$ NH_4OH, and add 10 ml of ammonium acetate buffer. Warm the solution in a water bath. Add to the warm solution 1 ml of $0.5\underline{N}$ sodium dichromate, and digest for several minutes. Add 1 ml of barium carrier solution, and digest again for several minutes.

Centrifuge, and transfer the supernate to a 40-ml centrifuge tube.

12. Wash the precipitate with 5 ml of distilled water. Centrifuge, and combine the supernate with that from Step 11. Discard the precipitate.
13. Adjust the solution to pH 7 with 6N NH$_4$OH, and add sufficient Na$_2$CO$_3$ to precipitate strontium carbonate [∿5-10 ml]. Centrifuge, and discard the supernate.
14. Dissolve the strontium carbonate precipitate in 3 ml of concentrated HCl. Add 20 ml of distilled water, and heat the solution in a water bath. Add 1 ml of scavenger solution, and make the mixture alkaline with 6N NH$_4$OH. Digest for several minutes. Then centrifuge, and transfer the supernate to a 40-ml centrifuge tube. Discard the iron and rare earth precipitate. RECORD THE TIME OF CENTRIFUGATION AS THE BEGINNING OF YTTRIUM 90 INGROWTH.
15. Add 5 ml of 3N Na$_2$CO$_3$ to the solution. Centrifuge, and discard the supernate.
16. Dissolve the strontium carbonate precipitate in 3 ml of concentrated HNO$_3$, and to it add 10 ml distilled water and 1 ml yttrium carrier solution. Store the solution for at least 5 days to allow sufficient yttrium 90 to grow in.
17. After an adequate period of time, transfer the solution to a 60-ml separatory funnel, using a minimum amount of distilled water. Add methyl orange indicator, and add 6N NH$_4$OH to the methyl orange endpoint. To the solution, add 10 ml of ammonium acetate buffer and 10 ml of 10% TTA in benzene. Shake for 5 minutes. [A mechanical shaker may be used.] RECORD THE TIME OF SEPARATION AS THE BEGINNING OF YTTRIUM 90 DECAY.
18. When the phases have separated, drain the aqueous layer into a clean 60-ml separatory funnel, and add 10 ml of 10% TTA in benzene. Shake for 5 minutes. Allow the phases to separate, and drain the aqueous phase into a 90-ml centrifuge tube.
19. Combine the organic layers from Steps 17 and 18 in one of the separatory funnels. Wash the empty funnel with 10 ml of ammonium acetate buffer, and add the wash to the funnel containing the organic layer. Shake for 2 minutes. When the phases have separated, combine the aqueous phase with that from Step 18.

20. Add 5 ml of 0.1N HNO_3 to the separatory funnel, and shake for 5 minutes. Transfer the aqueous phase to a 40-ml centrifuge tube.
21. Repeat Step 20 twice.
22. Heat the solution from Steps 20-21 in a water bath. Add 10 ml of 2N oxalic acid, and adjust the pH to 1.0-1.5 with concentrated NH_4OH. Digest for several minutes. Then centrifuge, and discard the supernatant solution.
23. Add warm distilled water to the precipitate to the 40-ml mark, and mix well. Centrifuge, and discard the supernatant solution.
24. Place a 2.4-cm diameter glass fiber filter on a stainless steel planchet, and weigh them together. Place the filter into the filtration apparatus.
25. Take the precipitate up in 10 ml of warm distilled water, and using more water, transfer it to the filter. Wash the precipitate in the filter with three 10-ml portions of absolute ethyl alcohol.
26. Carefully place the filter and its contents back onto the stainless steel planchet, and dry in an oven at 125° C for 20 minutes. Cool in a desiccator, and reweigh the planchet and filter. Calculate the chemical yield [recovery] of yttrium by dividing the weight of the precipitate by the weight of yttrium oxalate [$Y_2(C_2O_4)_3$] which should be obtained from 1 ml of yttrium carrier solution.
27. Transfer the filter and the precipitate to an appropriate sample holder. Count for the beta activity of yttrium 90 in a low background beta counter. RECORD THE DATE AND TIME OF COUNTING.
28. Heat the combined aqueous phases from Steps 18 and 19 in a water bath, and to the warm solution add 25 ml of 2N Na_2CO_3. Centrifuge, and discard the supernate.
29. Add 40 to 50 ml of distilled water to the strontium carbonate precipitate; mix well. Centrifuge, and discard the supernatant solution.
30. Place a 2.4-cm diameter glass fiber filter on a stainless steel planchet, and weigh them together. Place the filter into the filtration apparatus.
31. Using distilled water, quantitatively transfer the carbonate precipitate to the filter, and wash it with three 10-ml portions of water.
32. Carefully place the filter and its contents back onto the stainless steel planchet. Place under a heat lamp for 5-10 minutes, or until

dry. Cool in a desiccator, and reweigh the planchet with the filter. This weight is required for self-absorption corrections.

33. Transfer the filter with the strontium carbonate precipitate to the appropriate counting dish. Count for total radiostrontium beta activity in a low-background beta counter. RECORD THE DATE AND TIME OF COUNTING.

34. Dissolve the strontium carbonate from the filter using 1N HNO_3. Determine the strontium concentration by flame spectrophotometry (see 4.3.1), and compute the chemical yield.

Calculations

$$\text{strontium 90 activity (pCi/kg)} = \frac{A \times B \times C}{D \times E \times F \times G \times H \times I \times J \times K}$$

where A = net beta count rate of yttrium 90 (cpm)

B = sample volume (liters)

C = weight of total ash (grams)

D = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a glass fiber filter (cpm/pCi)

E = recovery of yttrium carrier [Step 26]

F = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from separation of yttrium [Step 17] to the time of counting [Step 27]

G = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from the end of the rare earth scavenge [Step 14] to the time of yttrium-strontium separation [Step 17]

H = recovery of strontium carrier [Step 34]

I = weight of ash dissolved (grams)

J = aliquot volume (liters)

K = weight of sample (kilograms)

$$\text{strontium 89 activity (pCi/kg)} = \frac{1}{D \times E}\left[\frac{A \times B \times C}{F \times G \times H \times I} - J(K + L \times M)\right]$$

where A = net beta count rate of total radiostrontium (cpm)

B = sample volume (liters)

C = weight of total ash (grams)

D = counter efficiency for counting strontium 89 as strontium carbonate mounted on a glass fiber filter (cpm/pCi)

E = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from collection of the sample to the time of counting [Step 33]

F = recovery of strontium carrier [Step 34]

G = weight of ash dissolved (grams)

H = aliquot volume (liters)

I = weight of total sample (kilograms)

J = activity of strontium 90 (pCi/kg)

K = counter efficiency for counting strontium 90 as strontium carbonate mounted on a glass fiber filter (cpm/pCi)

L = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on glass fiber filter (cpm/pCi)

M = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from the end of the rare earth scavenge [Step 14] to the time of yttrium-strontium separation

References

Goldin, A. S., R. J. Velten, and G. W. Frishkorn. "Determination of radioactive strontium". *Anal Chem 31*:1490-1492 (1959)

Murthy, G. K., L. P. Jarnagin, and A. S. Goldin. "A method for the determination of radionuclides in milk ash". *J Dairy Sci 42*:1276-1287 (1959)

TBP EXTRACTION METHOD – Bone Ash

This method is used for analyzing strontium 89 and strontium 90 in bone ash. No storage period is required for yttrium to grow in, since the yttrium 90 in the bone ash is assumed to be already in equilibrium with the strontium 90. The relatively direct quantitative extraction of the equilibrium amount of yttrium 90 makes the method fairly rapid, and an experienced analyst can complete several analyses in a day.

Principle of Method

Strontium and yttrium carriers are added to a sample of bone ash which has been dissolved in concentrated nitric acid. Strontium nitrate precipitates, while the yttrium remains in solution. The yttrium is extracted into tributyl phosphate, back-extracted into dilute nitric acid, and precipitated as the oxalate. The oxalate precipitate is weighed to determine the chemical yield, and is counted for the beta activity of yttrium 90.

The strontium nitrate is purified by washing with nitric acid, and is reprecipitated as the carbonate. The strontium carbonate is weighed and counted for total radiostrontium beta activity.

Strontium 89 activity is computed by difference between the activity of total radiostrontium and that of strontium 90 (as yttrium 90).

Reagents

ammonium acetate buffer: pH 5.0

ammonium hydroxide, NH_4OH: concentrated (15N)

carrier solutions:

- Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20 mg Ba^{+2} per ml
- Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 90 mg Sr^{+2} per ml
- Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 20 mg Y^{+3} per ml

ethyl alcohol, C_2H_5OH: absolute (100%)

methyl orange indicator: 0.1% w/v in alcohol

nitric acid, HNO_3: concentrated (16N), 14N, 1N, 0.1N

oxalic acid, $H_2C_2O_4 \cdot 2H_2O$: 2N

sodium carbonate, Na_2CO_3: 3N

sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$: 0.5N

sodium hydroxide, NaOH: 6N

tri-*n*-butyl phosphate [TBP], $(C_4H_9)_3PO_4$: pre-equilibrated with 14N HNO_3

Apparatus

desiccator

low-background beta counter

stainless steel suction-filtration apparatus (Tracerlab)

Procedure

1. In a 250-ml centrifuge bottle, dissolve a weighed sample of bone ash in 100 ml of hot concentrated HNO_3.
2. Add 1.0 ml each of strontium and yttrium carrier solutions, and cool in an ice bath. Centrifuge, and transfer the supernatant solution to a 250-ml separatory funnel. RECORD THE TIME AS THE BEGINNING OF YTTRIUM 90 DECAY.
3. Add 50 ml of pre-equilibrated TBP to the separatory funnel, and shake for 2-3 minutes. Drain the aqueous phase into a clean 250-ml separatory funnel.
4. Add to the aqueous phase, 50 ml of TBP, and shake again for 2-3 minutes. Drain off and discard the aqueous phase.
5. Combine the organic phases from Steps 3 and 4 in one of the separatory funnels. Wash the empty funnel with 50 ml of 14N HNO_3, and add it to the funnel containing the organic phases. Shake for 2-3 minutes. Drain off and discard the aqueous phase.
6. Add 50 ml of distilled water to the separatory funnel, and shake for 2-3 minutes. Drain the aqueous phase into a 250-ml centrifuge bottle.
7. Add 25 ml of 0.1N HNO_3 to the separatory funnel and shake for 2-3 minutes. Drain off the aqueous phase, and combine it with that from Step 6.
8. Repeat Step 7.
9. Add 10 ml of 2N oxalic acid to the centrifuge bottle. Heat the solution in a water bath, and using a pH meter adjust the pH to 1.0-1.5 with concentrated NH_4OH. Centrifuge, and discard the supernatant solution.
10. Transfer the oxalate precipitate to a 40-ml centrifuge tube using warm distilled water, and dilute to 40 ml with more warm water. Mix well. Centrifuge, and discard the supernate.
11. Place a 2.4-cm diameter glass fiber filter on a stainless steel planchet,

and weigh them together. Place the filter in the filtration apparatus.

12. Take the precipitate up in 10 ml of warm distilled water, and using more warm water transfer it to the filter. Wash the precipitate with three 10-ml portions of absolute ethyl alcohol.
13. Carefully place the filter containing the yttrium oxalate precipitate back onto the stainless steel planchet, and dry in an oven at 125° C for 20 minutes. Cool in a desiccator, and reweigh the planchet and filter with the precipitate. Calculate the chemical yield of the yttrium by dividing the weight of the precipitate by the weight of yttrium oxalate $[Y_2(C_2O_4)_3]$ which should be obtained from 1 ml of carrier solution.
14. Transfer the filter to an appropriate sample holder. Count for the beta activity of yttrium 90 in a low-background beta counter. RECORD THE DATE AND TIME OF COUNTING.
15. To the precipitate from Step 2, add 50 ml of concentrated HNO_3. Mix well, and cool in an ice bath. Centrifuge the mixture, and discard the supernate.
16. Repeat Step 15. RECORD THE TIME AS THE BEGINNING OF YTTRIUM 90 INGROWTH.
17. Dissolve the precipitate in a minimum amount of distilled water, and using a little more water, transfer the solution to a 90-ml centrifuge tube. Adjust the pH with 6N NH_4OH to a methyl orange endpoint. Add 10 ml of ammonium acetate buffer. Warm the solution in a water bath, and add 1 ml of 0.5N sodium dichromate and 1 ml of the barium carrier solution. Digest for several minutes. Centrifuge, and transfer the supernatant solution to a 90-ml centrifuge tube. Discard the precipitate.
18. Neutralize the solution with 6N NaOH. Heat the neutral solution in a water bath, and add 25 ml of 3N Na_2CO_3 to precipitate strontium carbonate. Centrifuge, and discard the supernatant solution.
19. Using distilled water, transfer the strontium carbonate precipitate to a 40-ml centrifuge tube and dilute to 40 ml. Mix well. Centrifuge the mixture, and discard the supernate.
20. Place a 2.4-cm diameter glass fiber filter onto a stainless steel planchet, and weigh them together. Place the filter into the filtration apparatus.

21. Take the precipitate up in 10 ml of distilled water, and using a little more water transfer it to the filter. Wash the precipitate with three 10-ml portions of distilled water.
22. Carefully place the filter containing the strontium carbonate precipitate back onto the stainless steel planchet, and dry under a heat lamp for 5-10 minutes. Cool in a desiccator, and reweigh the planchet and filter. [The weight of precipitate is needed to determine self-absorption.]
23. Transfer the filter to an appropriate sample holder. Count for the beta activity of total radiostrontium in a low-background beta counter. RECORD THE DATE AND TIME OF COUNTING.
24. Dissolve the strontium carbonate precipitate from the filter using $1\underline{N}$ HNO_3, and dilute to volume in a 100-ml volumetric flask. Measure the strontium concentration by flame photometry (see 4.3.1) and compute the chemical yield.

Calculations

$$\text{strontium 90 activity (pCi/gram ash)} = \frac{A}{B \times C \times D \times E}$$

where A = net beta count rate of yttrium 90 (cpm)
B = weight of ash (grams)
C = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a glass fiber filter (cpm/pCi)
D = recovery of yttrium carrier [Step 13]
E = correction factor $e^{-\lambda t}$ for yttrium 90 decay, where t is the time from separation of the yttrium [Step 2] to the time of counting

$$\text{strontium 89 activity (pCi/gram ash)} = \frac{1}{B \times C}\left[\frac{A}{D \times E} - F(G + H \times I)\right]$$

where A = net beta count rate of total radiostrontium (cpm)
B = counter efficiency for counting strontium 89 as strontium carbonate mounted on a glass fiber filter (cpm/pCi)

C = correction factor $e^{-\lambda t}$ for strontium 89 decay, where t is the time from collection of the sample to the time of counting

D = recovery of strontium carrier [Step 24]

E = weight of ash (grams)

F = strontium 90 activity (pCi/gram ash)

G = counter efficiency for counting strontium 90 as strontium carbonate mounted on a glass fiber filter (cpm/pCi)

H = counter efficiency for counting yttrium 90 as yttrium oxalate mounted on a glass fiber filter (cpm/pCi)

I = correction factor $1-e^{-\lambda t}$ for yttrium 90 ingrowth, where t is the time from separation of the strontium [Step 16] to the time of counting [Step 23]

Reference

Velten, R. J. and A. S. Goldin. "Simplified determination of strontium-90. Preferential extraction of yttrium with tributyl phosphate". *Anal Chem 33*:128-131 (1961)

7.2.3 Lead 210 — Bismuth 210

ION-EXCHANGE SEPARATION

This procedure is for the determination of lead 210 and bismuth 210 in a dissolved ash. It has been applied to the determination of these nuclides in ashed samples of bone, tobacco, food, and other biological materials.

Principle of Method

Lead and bismuth carriers are added to the dissolved ash, and the solution is passed through an anion-exchange resin column. The lead and bismuth are adsorbed onto the resin. The lead is eluted first with dilute hydrochloric acid, and then bismuth is eluted with dilute sulfuric acid. The bismuth is precipitated as the oxychloride, which is counted for the beta activity of bismuth 210.

Lead is precipitated as the sulfide, dissolved in hydrochloric acid, and again adsorbed onto the anion resin. It is then eluted with dilute hydrochloric acid and precipitated as the chromate. The lead chromate is counted for beta activity to follow the decay of lead 210 to bismuth 210.

Reagents

acetic acid, CH_3COOH: glacial (17N)
ammonium hydroxide, NH_4OH: concentrated (15N)
anion-exchange resin: Dowex 1-X8 (Cl^- form, 50-100 mesh)
carrier solutions:
  Bi^{+3} as bismuth oxide, Bi_2O_3: 15 mg Bi^{+3} per ml
  Pb^{+2} as lead nitrate, $Pb(NO_3)_2$: 20 mg Pb^{+2} per ml
ethyl alcohol, C_2H_5OH: absolute (100%)
hydrochloric acid, HCl: concentrated (12N), 6N, 1.8N, 0.1N, 0.05N
hydrogen sulfide, H_2S: gas
potassium dichromate, $K_2Cr_2O_7$: 1N
sulfuric acid, H_2SO_4: 2N

Apparatus

anion-exchange system: a glass column, 10 mm in diameter and 30 cm in length, having a coarse fritted glass disk or glass-wool plug above the stopcock. Twenty ml of the Dowex 1-X8 resin are placed in the column and washed with 1.8N HCl prior to use.

desiccator

stainless steel suction-filtration apparatus (Tracerlab)

Procedure

1. Dissolve the weighed sample of ash in a minimum volume of 6N HCl. To the dissolved ash, add 1.0 ml each of bismuth and lead carrier solutions, and dilute to 400 ml.
   [Note: The solution should be 1.8N HCl after dilution.]
2. Pass the solution over the anion-exchange resin at a flow rate of approximately 2 milliliters per minute (ml/min). Collect the effluent in an 800-ml beaker.
3. Pass 125 ml of 0.05N HCl over the resin at 2 ml/min to elute the lead, and combine this solution with the effluent from Step 2. RECORD THE MIDPOINT OF THE ELUTION PERIOD AS THE BEGINNING OF BISMUTH 210 DECAY.
4. Pass 150 ml of 2N H_2SO_4 through the column to elute the bismuth. Collect the eluate in a 400-ml beaker.
   [Note: Process the column for re-use in Step 14 by passing 1.8N HCl through it at 2 ml/min until the pH of the effluent reaches 2.]
5. Using a pH meter, adjust the eluate to pH 5 by adding concentrated NH_4OH. Add 2 ml of 6N HCl, and dilute to 350 ml with distilled water. Digest the bismuth oxychloride precipitate on a hot plate for 30 minutes.
6. Place a 2.4-cm diameter glass fiber filter onto a stainless steel planchet, and weigh together. Place the filter in the filtration apparatus.
7. Filter the solution. Wash the precipitate with hot distilled water. Complete the wash with 10 ml of absolute ethyl alcohol.
8. Carefully place the filter back onto the stainless steel planchet, and dry in an oven at 110° C for 30 minutes. Cool in a desiccator, and reweigh the planchet and filter with the precipitate. Calculate the chemical yield of bismuth by dividing the weight of the precipitate by the weight of bismuth oxychloride [BiOCl] which should be obtained from 1 ml of carrier solution.

9. Transfer the filter to an appropriate counting dish or planchet, and count for the beta activity of bismuth 210 in a low-background beta counter.

10. Using a pH meter, add concentrated NH_4OH to the lead solution from Step 3 to bring the pH to 7. Then add 8 ml of concentrated HCl, and dilute to 1 liter.

    [Note: The solution is now 0.1N HCl.]

11. Heat the solution on a hot plate, and slowly pass H_2S gas through the solution for several minutes to precipitate lead sulfide [PbS]. Filter the solution through a glass fiber filter, using a Buchner funnel. Wash the precipitate with distilled water.

12. Place a 100-ml beaker under the funnel, and dissolve the precipitate into the beaker by passing a minimum amount of warm 6N HCl through the filter. Evaporate the filtrate to dryness.

13. Dissolve the residue in 20 ml of 1.8N HCl, and filter the solution through Whatman No. 541 filter paper. Wash the filter paper and contents with 1.8N HCl; then discard the filter paper.

14. Pass the filtrate over the regenerated anion-exchange resin at a flow rate of approximately 2 ml/min. Wash the resin with 60 ml of 1.8N HCl, and discard the effluent and wash solutions.

15. Pass 150 ml of 0.05N HCl through the column to elute the lead, collecting the eluate in a 250-ml beaker. RECORD THE TIME AS THE BEGINNING OF BISMUTH 210 INGROWTH.

16. Add 1 ml of glacial acetic acid, and using a pH meter, adjust the pH to 5 with concentrated NH_4OH. Heat the solution to boiling, and add 1 ml of 1.0N potassium dichromate.

17. Place a 2.4-cm diameter glass fiber filter onto a stainless steel planchet, and weigh together. Place the filter into the filtration apparatus.

18. Filter the solution, and wash the precipitate with distilled water and finally with 10 ml of absolute ethyl alcohol.

19. Carefully place the filter back onto the stainless steel planchet, and dry in an oven at 110° C for 30 minutes.

20. Cool in a desiccator, and reweigh the planchet and paper with the precipitate. Calculate the chemical yield of lead by dividing the weight of the precipitate by the weight of lead dichromate [$PbCr_2O_7$] which should

be obtained from 1.0 ml of lead carrier solution.

21. Transfer the filter paper to an appropriate counting dish. Count in a low-background beta counter at 2- to 3-day intervals over a period of two weeks to follow the ingrowth of bismuth 210 from the lead 210. Interference from other bismuth isotopes can then be removed mathematically because of their different half-lives (^{210}Bi ∿5 days; ^{214}Bi ∿20 minutes).

Calculations

$$\text{bismuth 210 activity (pCi)} = \frac{A}{B \times C \times D}$$

where A = net count rate of bismuth 210 (cpm) [from Step 9]

B = counter efficiency for counting bismuth 210 as bismuth oxychloride mounted on a glass fiber filter (cpm/pCi)

C = recovery of bismuth carrier [Step 8]

D = correction factor $e^{-\lambda t}$ for bismuth 210 decay, where t is the time from midpoint of the elution period [Step 3] to the time of counting [Step 9]

$$\text{lead 210 activity (pCi)} = \frac{A}{B \times C \times D}$$

where A = net count rate of bismuth 210 (cpm) [from Step 21]

B = counter efficiency for counting bismuth 210 as bismuth-lead chromate mounted on a glass fiber filter (cpm/pCi)

C = chemical yield of lead

D = correction factor $1-e^{-\lambda t}$ for ingrowth of bismuth 210, where t is the time from the second elution of lead from the column [Step 15] to the time of counting

Reference

Baratta, E. J., E. S. Ferri, and T. C. Reavey. *Analysis of Environmental Samples, Supplementary Chemical and Radiochemical Procedures.* Northeastern Radiological Health Laboratory Report No. NERHL-65-4, U. S. Department of Health, Education and Welfare, Public Health Service, Winchester (1965)

7.2.4 Polonium 210

PLATING ON SILVER

This procedure is used to analyze polonium 210 in samples which have been prepared by wet-ashing techniques. It requires approximately four to eight hours to complete.

Principle of Method

The dissolved sample is neutralized and then made 0.5N in hydrochloric acid. Ascorbic acid is added to immobilize any iron which may be present. The acid solution is placed in a plating cell, warmed to 95° C in a water bath, and stirred for several hours to induce spontaneous plating of the polonium onto a silver disk at the base of the cell. The ascorbic acid prevents simultaneous plating of iron. The silver disk is removed from the cell, washed, dried, and counted in an internal proportional counter for the alpha activity of polonium 210.

Reagents

ascorbic acid, $C_6H_8O_6$: crystals
hydrochloric acid, HCl: concentrated (12N), 0.5N
sodium hydroxide, NaOH: 6N

Apparatus

plating cell: The bottom of a plastic nursing bottle is removed, the bottle is inverted, and a silver disk, cut to size, is placed in the screw cap between two gaskets made by cutting the flange off the nipples supplied with the bottle. (See Figure 7.2-1)

silver disks: Cut to fit the plating cell.

[Note: A metal die is used to cut circles from 0.01-inch thick silver.]

internal proportional counter for alpha counting

motor-driven glass stirring rod

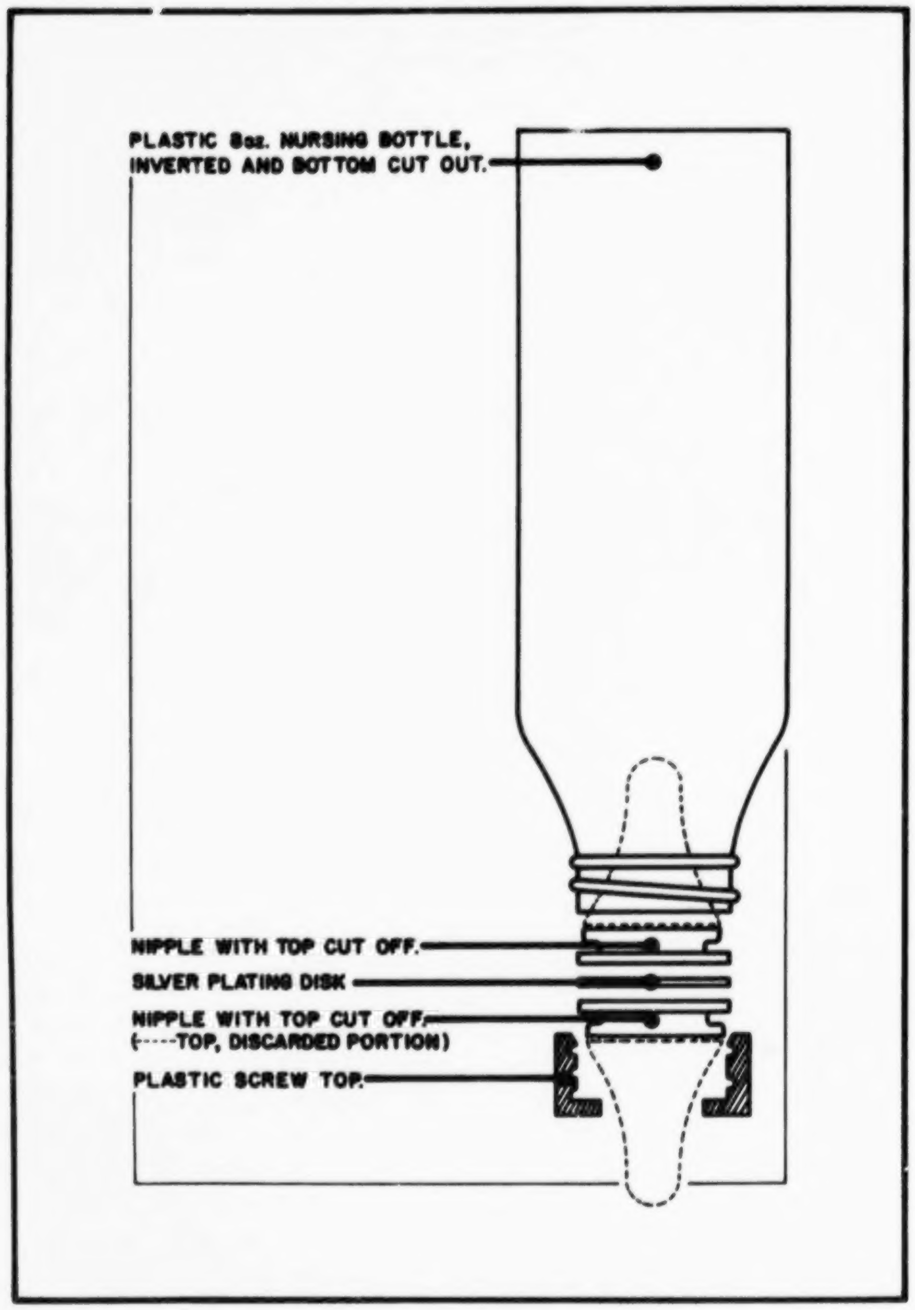
PLASTIC 8oz. NURSING BOTTLE, INVERTED AND BOTTOM CUT OUT.
NIPPLE WITH TOP CUT OFF.
SILVER PLATING DISK
NIPPLE WITH TOP CUT OFF.
(----TOP, DISCARDED PORTION)
PLASTIC SCREW TOP.

Figure 7.2-1 Plating cell for polonium 210 determination

Procedure

1. Adjust the acid solution containing the sample to pH 7 with 6N NaOH.
2. Adjust the HCl concentration of the solution to 0.5N. [The sample volume should not exceed 250 ml.] Add approximately 1 gram of ascorbic acid.
3. Transfer the solution to a plating cell, and place the cell in a 95° C water bath.
4. Stir the solution for 4 hours, using a motor-driven glass stirring rod. The stirring rod should be placed into the solution so that the tip is about ½" above the silver disk.
5. Using 0.5N HCl, transfer the solution to a 400-ml beaker. Rinse the stirrer and plating cell with 0.5N HCl, and add the rinse to the solution in the beaker.
6. Remove the silver disk from the cell, and wash with distilled water. Dry under a heat lamp, cool to room temperature, and count for the alpha activity of polonium 210, using an internal proportional counter.

Calculation

$$\text{polonium 210 activity (pCi)} = \frac{A}{B \times C}$$

where A = net alpha count rate of polonium 210 (cpm)

B = counter efficiency for counting polonium 210 plated on a silver disk (cpm/pCi)

C = plating efficiency (95%)*

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* The efficiency for plating polonium by this technique was determined by use of a tracer, and was found to agree with that reported by Black (1)

References

Cited Reference

1. Black, S. C. "Low level polonium determination of tissue and urine". University of Rochester Report No. UR-463, Rochester (1956)

Uncited Reference

Radford, E. P., Jr., V. R. Hunt, and D. Sherry. "Analysis of teeth and bones for alpha-emitting elements". *Radiation Research 19*:298-315 (1963)

7.2.5 Radium 226

RADON 222 EMANATION

The samples covered by SECTION 7 can be analyzed for radium 226 by a radon 222 emanation procedure. The sample should be put into solution by one of the techniques described in 7.1 PREPARATION OF SAMPLES and one of the procedures described in SECTION 4. FOOD (part 4.2.4) should be followed to determine the radium 226 content of the solution.

7.2.6 Gamma Emitters

Gamma emitters in soft tissues, blood plasma, hair, bone, soil, and silt samples are routinely determined by gamma spectrometry as described in SECTION 1. INSTRUMENTATION. Cesium 137 and potassium 40 are routinely analyzed in soft tissues, and cesium 137, zinc 65, cobalt 60, manganese 55, and potassium 40 are of interest in samples of soil and silt. Other nuclides originating from reactor wastes or weapons testing are also determined when present.

Soft tissues, blood plasma, and hair samples may be placed in suitable containers without prior analysis. Nonliquid or noncompressible bulky samples are prepared for gamma spectrometry by concentrating them according to the procedures described in 7.1 PREPARATION OF SAMPLES. If bone is to be analyzed for cesium 137, the sample should be ashed at a temperature no higher than 450° C before being counted.

7.3 DETERMINATION OF STABLE ELEMENTS

7.3.1 Strontium Carrier

The chemical yield or recovery of strontium in radiochemical methods for determination of total radiostrontium or strontium 89 can be measured gravimetrically, as indicated in the steps of procedures for determination of these materials (see 7.2.2). Strontium carrier recovery can also be determined by flame spectrophotometry if the necessary equipment is available. The stepwise procedure for flame photometric analysis of strontium carrier in the dissolved ash of environmental samples is identical to that given for food samples in SECTION 4, part 4.3.1.

7.3.2 Calcium

After being put into solution by the procedures presented in 7.1 PREPARATION OF SAMPLES, environmental samples can be analyzed for stable calcium by the PERMANGANATE TITRATION PROCEDURE, part 4.3.2 of SECTION 4. FOOD.

7.3.3 Potassium

Because potassium 40 occurs as a constant proportion of natural potassium, stable potassium can be determined from the measured amount of potassium 40 present in environmental samples. Potassium 40 is measured by gamma spectrometry as described in SECTION 1. INSTRUMENTATION, parts 1.1.3 and 1.1.4.

APPENDIX A

GLOSSARY OF TERMS AND ABBREVIATIONS

CONTENTS

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A.1 ABBREVIATIONS AND SYMBOLS A-2

A.2 DEFINITION OF TERMS AND LABORATORY PRACTICE A-4

A.3 REFERENCES A-12

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APPENDIX A

A.0 INTRODUCTION

This Appendix has been included to assist the reader in understanding the abbreviations, symbols, and terms common to the radioassay procedures which appear in this manual. Many of the terms will be understood by anyone who has read the chapter on laboratory procedure included in most elementary quantitative analysis textbooks. Some will be familiar to those having basic knowledge of radiation physics. Others will be recognized as terms for which a traditional meaning has been extended to have a special meaning in certain contexts. A few, however, fall into the category of laboratory colloquialisms. Although these should be avoided in formal writing, they have been allowed to a limited extent, particularly in the step-by-step procedures.

All definitions have been restricted to the context in which the terms are used in this manual. APPENDIX A is neither a dictionary nor a complete glossary of terms. The rapid growth and development of scientific and technologic knowledge precludes publication of any single complete glossary of current technical terms, but for those in search of one, the publications listed in the Bibliography to this Appendix may be of value.

A.1 ABBREVIATIONS AND SYMBOLS

A	activity, unless otherwise specified
AC	alternating current
α	alpha; as alpha particles, energy of alpha particles, etc.
$\sim$	approximately
BP	boiling point
β	beta; as beta particles, beta radiation, etc.
C	centigrade
Ci	curie(s)
cm	centimeter(s); 10^{-2} meter
cm^2	square centimeter(s)
cph	count(s) per hour
cpm	count(s) per minute
d	day(s), in reference to half-life
DC	direct current
dpm	disintegration(s) per minute
$^\circ$	degree(s)
E	energy, unless otherwise specified
E_{max}	maximum energy
e.g.	*exempli gratia;* for example
et al.	*et alli;* and others
etc.	*et cetera;* and so forth
F	fahrenheit
ft	foot (feet)
ft^3	cubic foot (feet)
FW	formula weight
g	gram(s)
GM	Geiger-Mueller
γ	gamma; as gamma rays, gamma energy, etc.
h	hour(s), in reference to half-life
i.e.	*id est;* that is
in.	inch(es): also, "
in^2	square inch(es): also, sq in.
in^3	cubic inch(es): also, cu in.
Kev	kiloelectron volt(s); 10^3 electron volts
kg	kilogram(s); 10^3 grams
l.	liter(s) (rarely abbreviated)
λ	lambda; 1. Decay constant. 2. Microliter; 10^{-3} milliliter.
$\underline{M}$	molar, as applied to concentration of a substance in a solution
ma	milliampere(s); 10^{-3} ampere
max	maximum
meq	milliequivalent(s)
Mev	million electron volts
mg	milligram(s); 10^{-3} gram
min	minute(s)
ml	milliliter(s); 10^{-3} liter
mm	millimeter(s); 10^{-3} meter
μCi	microcurie(s); 10^{-6} curie
μg	microgram(s); 10^{-6} gram
-	minus

N	normal, as applied to concentration of a substance in a solution
nCi	nanocurie(s); 10^{-9} curie
pCi	picocurie(s); 10^{-12} curie
ppm	part(s) per million
/	per; divided by
%	percent; per hundred
+	plus
±	plus or minus, expressing a range
rpm	revolution(s) per minute
s	second(s): also, sec(s)
sp gr	specific gravity
σ	sigma; standard deviation
t	time, in hours, days, etc.
$T_{\frac{1}{2}}$	half-life, equal to 0.693 divided by the decay constant
V	volt(s)
v/v	volume to volume; by volume
wt	weight
w/v	weight to volume; by weight
y	year(s), in reference to half-life

A.2 DEFINITION OF TERMS AND LABORATORY PRACTICE

aliquot	*adj.*: 1. *Chem.* - fractional, as an aliquot portion of a chemical solution, implying a measured part. 2. *Math.* - contained an exact number of times in something else (*e.g.*, 5 is an aliquot part of 15) *n.*: an aliquot part; a measured portion of the whole
analytical balance	*n.*: a balance capable of weighing to 0.1 milligram
aspirate	*v.t.*: 1. to draw off or move fluids by suction; to draw off fluids with an aspirator. 2. to draw air through
background	*n.*: the sum of phenomena always present to affect physical apparatus or instrument response in the absence of a sample, above which a phenomenon must show itself in order to be measured. The term is applicable to radioactivity measurements (*e.g.*, counts or currents from cosmic rays), photometric measurements, etc., and is sometimes used in the sense of "blank determination".
blend	*v.t.*: to break down or mix to form a homogenous mass so that any portion of the mass is identical in composition, form, etc. to any other portion *n.*: a homogenous mass or mixture
carrier	*n.*: a substance in ponderable amount which will carry a trace substance with it through a chemical or physical process. If carriers are of the same element as the trace substance (*e.g.*, Sr for ^{90}Sr), they are called *isotopic* carriers; if of a chemically similar element (*e.g.*, Ba for Ra), they are called *non-isotopic* carriers.
carrier recovery	*n.*: that fraction or portion of a carrier substance initially added which is finally recovered in the final product; - esp., that which is finally recovered in a sample to be counted. Carrier recovery may be determined by weight, by flame spectrophotometry, or by other chemical or physical means.

centrifuge	*n.*: an apparatus for the separation of substances by centrifugal force *v.*: to separate by centrifugal force substances of different densities
chemical yield	*n.*: the quantity of a chemical product, such as a precipitate, obtained as a result of a chemical process expressed as a fraction or percentage of the amount theoretically obtainable [see yield]
count	*n.*: 1. the external indication of a device designed to enumerate ionizing events. Count may refer to a single detected event or to the total number of events registered in a given period of time; loosely, a disintegration, an ionizing event, or a voltage pulse. 2. *(Colloq.)* a counting rate; the number of counts observed per unit time *v.t.*: to measure the radioactivity of a substance by enumerating the ionizing events it produces in a detector during a known time interval
count rate	*n.*: the number of ionizing events detected per unit time. *Background* count rate is the number of ionizing events registered by the detector system in unit time when no sample is present. *Net* count rate is the number of ionizing events registered by the detector per unit time in the presence of the sample excluding the background count rate.
daughter	*n.*: any radioactive or stable nuclide produced by the radioactive disintegration of a radionuclide, either directly or as the result of a series of transformations in a radioactive decay chain (*e.g.*, ^{90}Y is the daughter of ^{90}Sr; ^{218}Po is a daughter of ^{222}Ra) *adj.*: designating a relationship in a radioactive decay series, as daughter product
decant	*v.t.*: to pour off gently; usually, to pour off the clear liquid above a settled or centrifuged residue
dry	*v.t.*: to remove the moisture from; to make devoid of moisture. Rigorously, *drying* means treatment in an oven at a temperature between 100° C and 110° C, but the term is extended to include the use of a hot plate or an infra-red lamp. *Drying* implies a more gentle treatment than igniting or baking. *adj.*: free of moisture; not wet or damp

dryness	*n.*: the state or quality of being dry. *Take to* dryness implies the removal of liquid, but not prolonged baking.
equilibrate	*v.t.*: to bring into a state of equilibrium. The solute in one of two immiscible solvents is equilibrated, *i.e.*, brought into an equilibrium distribution between the two solvents, by shaking the immiscible solvents or solutions together.
equilibrium	[see radioactive equilibrium]
extract	*v.t.*: to obtain or withdraw from a composite substance by any chemical or mechanical process, as by distillation, dissolution, etc. *n.*: that which has been extracted; a preparation of the material extracted, usually in a concentrated form
extraction	*n.*: the process of extracting or separating a certain substance from a mixture usually by means of solvents; - esp., a process of separating or isolating a substance in solution by virtue of its varying degree of solubility in different solvents
gamma scan	*n.*: *(Colloq.)* a spectrum of gamma energies, usually in printed or plotted form, as that obtained from gamma pulse height analysis *v.*: *(Colloq.)* the process of obtaining a gamma spectrum; the process of examining a sample for gamma emitters by pulse height analysis or spectrometry
homogenate	*n.*: that which has been homogenized; the homogeneous mass resulting from blending or homogenizing
homogenized	*adj.*: uniformly blended; made homogenous; [see blend] - *Special:* with milk, to indicate treatment by a technical process using high temperature and pressure to break up and uniformly disperse fat globules

ingrowth	*n.*: *(Colloq.)* the formation of a daughter product from its radioactive parent (*e.g.*, ^{90}Y from ^{90}Sr), usually applied to accumulation of the daughter product in a solution in which the radioactive parent has been isolated
ion exchange	*n.*: a chemical process involving the reversible interchange of ions at a phase boundary, usually between a solution and a particular solid material, such as an ion-exchange resin *adj.*: ion-exchange The special terminology used in reference to this process is defined in the context of the following statement. < A solution is poured through an *ion-exchange column* which is a tube containing an *ion-exchange resin* [see Figure 3.2-1 of SECTION 3]. The solution that comes through is the *effluent* (general term). The material retained on the column (on the resin) is the *adsorbate*. The adsorbate is *eluted* from the resin by passage of a reagent solution, the *eluant*, through the column. The effluent from the process of *elution* is the *eluate*. The column (resin) is *washed* by pouring a reagent wash solution through it, usually to restore the resin to its original ionic state. >
isotope	*n.*: one of two or more species of atoms of the same element that have the same atomic number, occupy the same position in the periodic table, and are nearly identical in chemical behavior but differ in atomic mass or mass number and so behave differently in radioactive transformations. radioisotope: a radioactive isotope
nuclide	*n.*: a species of atom characterized by the constitution of its nucleus, *i.e.*, by the number of protons and neutrons and the energy content; an atom of specified atomic and mass numbers; (*e.g.*, the different isotopes of an element are composed of nuclides having the same atomic number but different mass numbers) radionuclide: a radioactive nuclide
parent	*n.*: a radionuclide that disintegrates directly or through a series of transformations to yield a specified nuclide, the daughter; (*e.g.*, ^{238}U is the parent of all members of the uranium series

	including the stable end product ^{206}Pb) *syn.*: radioactive precursor
purity	*n.*: the state of being free from mixture or contact with contaminants, pollutants, or other substances which will interfere with a chemical process or end product
qualitative	*adj.*: 1. showing the nature or identity of any or all elements or materials in a compound or mixture without reference to the quantities present, not quantitative. 2. *(Colloq.)* improperly used to describe an analysis or analytical result in the sense of *approximate* or *rough*
quantitative	*adj.*: 1. determining or showing the quantity or amount of any or all elements in a given compound or solution or the components of a mixture. 2. complete, as quantitative transfer
radioactive equilibrium	*n.*: the state attained among the members of a radioactive decay series or part of a series in which each parent has a longer half-life than its daughter, when the ratios between the activities of successive members remain constant, *i.e.*, the ratio of parent activity to daughter activity is independent of time. *Secular equilibrium* is approached, but never completely attained, when the half-life of the parent is so long that there is no appreciable change in the amount of parent during the time required for later products to attain equilibrium, so that equal numbers of atoms of all members of the series disintegrate in unit time, *i.e.*, all members of the series exhibit the same activity (*e.g.*, ^{226}Ra and its series through ^{214}Bi). *Transient equilibrium* will be reached if the half-life of the parent is so short that the quantity of parent decreases appreciably during the given time interval, so that all members of the series decrease in amount or activity exponentially with the half-life of the parent (*e.g.*, ^{222}Rn and its series through ^{214}Bi; ^{140}Ba to ^{140}La).

reagent grade	*adj.* or *n.*: conforming to American Chemical Society specifications for reagent chemicals as published in *Reagent Chemicals; American Chemical Society Specifications, 1960* by the American Chemical Society Committee on Analytical Reagents
recovery	*n.*: the quantity of a product obtained as a result of a reaction or process or series of these, expressed as a fraction or percentage of that theoretically obtainable from the quantity of one of the chemicals or radioactive components initially present or added [see carrier recovery]
rinse	*v.*: to treat a container with water or other suitable liquid to facilitate a quantitative transfer, usually a mechanical action *n.*: the liquid agent used to facilitate a quantitative transfer
scavenger	*n.*: a substance added to remove impurities or to overcome the undesirable effects of one or more of the substances contained in a mixture (*e.g.*, Fe, Ce, and Zr are often used as scavengers to remove rare earths by precipitation.)
spectrometry	*n.*: the art or process of using a spectrometer, of measuring spectra, or of determining wavelengths or energies of the various radiations; implying measurement, as a spectrometer is a spectroscope fitted for measurements of the spectra observed with it; also, pulse height analysis
standard	*n.*: an established measure of volume, quantity, quality, or value; - esp., a material of known composition which closely resembles in chemical and physical characteristics the sample to be analyzed and which is used for calibration *adj.*: having the accuracy or authority of a standard, serving as a gauge or model, as a standard weight
standard, radioactive	*n.*: a sample of radioactive material in which the number and type of radioactive atoms at a given reference time is known; a standard against which radiation measurement equipment can be calibrated
supernate	*n.*: a supernatant liquid or substance; - esp., a liquid from which a precipitate has been thrown down; also, supernatant

surveillance	*n.*: a continuous scrutiny or inspection of an area, environment, population, etc.; - esp., a continuous program of detecting, measuring, recording, and evaluating the condition of an area, environment, or population with respect to its content of radioactive material or its exposure to radiation *adj.*: pertaining to surveillance
transfer	*v.*: to convey from one place to another; - esp., to remove a measured or known quantity of a sample from one container to another, as with a pipette *n.*: the act of making a transfer [see quantitative]
wash	*v.*: to cleanse, purify by immersing in or applying water or other liquid, often accompanied by agitation; - esp., to remove mother liquor from a precipitate by thorough mixing with water or other suitable liquid followed by separation by centrifugation or filtration. Treatment with several small portions of the liquid is much more effective than with one or two larger portions. Solution and reprecipitation is sometimes more effective in purifying than is washing. *n.*: the liquid used to cleanse or purify
water, deionized	*n.*: reagent water prepared by passage through mixed-bed ion-exchange resins in the H^+ and OH^- forms
water, demineralized	*n.*: deionized water
water, distilled	*n.*: reagent water prepared by distillation
water, reagent	*n.*: water suitable for use in the analytical laboratory, prepared from tap water by distillation or deionization to contain not more than 5.0 parts per million of dissolved solids and to have an electrical conductivity of not more than 8 micromhos per centimeter at 25° C. Reagent water as defined above is suitable for the procedures of this manual; however, high purity reagent water should meet the more stringent American Chemical Society specifications for distilled water.

weightless	*adj.*: having such a small mass that it may be neglected, as for self-absorption corrections. A sample weighing less than 0.1 milligram per square centimeter may be considered weightless in determining its beta activity.
yield	*n.*: the quantity of a product obtained as a result of a reaction or process or series of these expressed as a fraction or percentage of that theoretically obtainable from the quantity of one of the chemical or radioactive components initially present or added [see carrier recovery]

A.3 REFERENCES

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APPENDIX B

INSTRUCTIONS FOR PREPARING REAGENTS

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APPENDIX B
INSTRUCTIONS FOR PREPARING REAGENTS

B.0 INTRODUCTION

For the information and, perhaps, convenience of the reader and user of this procedures manual, the reagent preparations routinely used by National Center for Radiological Health laboratories are presented in APPENDIX B. They are listed alphabetically in four groups — Standards, Carriers, Tracers, and Other Reagents — along with the chemical formulas and formula weights (FW) of the compounds from which they are prepared. Formula weights were computed from the 1961 values of atomic weights based on the isotope ^{12}C.(1) Instructions for preparing the reagents are listed after the name in the order of decreasing concentration.

One important prerequisite for maintaining precision and accuracy of analytical results is use of carefully prepared, high quality reagents. Whether the instructions of APPENDIX B or other valid methods of preparing reagents are used is immaterial. It is essential, however, that the preparation method for a given reagent be consistant, that the amount prepared at one time be used well within the shelf life of the reagent, and that each solution be labeled and stored in the proper manner. Unless otherwise stated, water and chemicals should conform to the American Chemical Society's specifications for reagent water and chemicals(2).

It is assumed that the user of this manual will observe the standard rules of laboratory safety and will be prepared to administer first aid when necessary.

B.1 STANDARD SOLUTIONS

Calcium standard solution $CaCO_3$ FW 100.089

10 mg Ca^{+2} per ml

Dissolve 2.50 g $CaCO_3$ in a minimum volume of HCl and dilute to 1000 ml with distilled water.

Potassium blank solution NaCl FW 58.443; $CaCO_3$ FW 100.089; $MgCl_2$ FW 95.218

3500 ppm Na^+
8000 ppm Ca^{+2}
120 ppm Mg^{+2}

Dissolve 8.8972 g NaCl, 19.9781 g $CaCO_3$ and 0.4700 g $MgCl_2$ in 900 ml 0.5N HCl, and dilute to 1000 ml with 0.5N HCl. All reagents should be analytically dried before weighing.

Potassium standard solution KCl FW 74.555

1000 ppm K^+

Dissolve 1.9067 g dry KCl in 900 ml 0.5N HCl, and dilute to 1000 ml with 0.5N HCl.

Potassium permanganate $KMnO_4$ FW 158.038

0.05N standardized

Dissolve 1.6 g $KMnO_4$ in 900 ml distilled water. Heat to near boiling for 20-30 minutes and cool overnight. Dilute to 1000 ml and filter through Whatman No. 1 filter paper. Standardize the solution at least once each week against sodium oxalate, NBS Primary Standard.

Standardization

$$\underline{N}\ KMnO_4 = \frac{\text{mg } Na_2C_2O_4 \text{ standard}}{(\text{ml } KMnO_4)(\text{meq wt } Na_2C_2O_4)}$$

Weigh in triplicate 80.0 mg dry $Na_2C_2O_4$ (Primary Standard). Dissolve each in 25 ml 5% H_2SO_4. Heat to just below boiling, and titrate with $KMnO_4$ to the first faint pink endpoint which persists for at least 30 seconds.

Potassium phosphate, monobasic KH_2PO_4 FW 136.090

standard phosphorus solution
(0.1 mg P per ml)

Use NBS Primary Standard, or dissolve 0.4394 g KH_2PO_4 in distilled water and dilute to 1000 ml.

Sodium oxalate $Na_2C_2O_4$ FW 133.999

standard oxalate solution	NBS Primary Standard

Standard oxalate solution

(see Sodium oxalate)

Standard phosphorus solution

(see Potassium phosphate)

Strontium standard solution

dilute carrier	For flame-photometric determination of strontium carrier recovery, dilute 1 ml of the strontium carrier solution used in the procedure to 50 ml with deionized distilled water.
0.40 mg Sr^{+2} per ml	Dilute 1.0 ml strontium carrier solution (20 mg Sr/ml) to 50.0 ml using deionized distilled water.
0.02 mg Sr^{+2} per ml	Dilute 2.0 ml strontium standard solution (0.40 mg Sr/ml) to 40 ml using deionized distilled water.
0.015 mg Sr^{+2} per ml	Dilute 1.5 ml strontium standard solution (0.40 mg Sr/ml) to 40 ml using deionized distilled water.
0.010 mg Sr^{+2} per ml	Dilute 1.0 ml strontium standard solution (0.40 mg Sr/ml) to 40 ml using deionized distilled water.
0.005 mg Sr^{+2} per ml	Dilute 0.5 ml strontium standard solution (0.40 mg Sr/ml) to 40 ml using deionized distilled water.

Strontium carrier solution, standardized

(see B.2 CARRIER SOLUTIONS)

Tritium standard solution

~10^4 dpm per ml	Using triple-distilled tritium-free water, dilute a commercially obtained tritated water standard to obtain a known activity of approximately 10^4 disintegrations per minute per milliliter.

B.2 CARRIER SOLUTIONS

Barium as barium nitrate $Ba(NO_3)_2$ FW 261.38

20 mg Ba^{+2} per ml	Dissolve 38.1 g $Ba(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16N HNO_3 and dilute to 1000 ml with distilled water.
10 mg Ba^{+2} per ml	Dissolve 19.0 g $Ba(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16N HNO_3 and dilute to 1000 ml with distilled water.
7 mg Ba^{+2} per ml	Dissolve 13.3 g $Ba(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16N HNO_3 and dilute to 1000 ml with distilled water.
1 mg Ba^{+2} per ml	Dissolve 1.9 g $Ba(NO_3)_2$ in 900 ml distilled water. Add 1 ml 16N HNO_3 and dilute to 1000 ml with distilled water.
Standardization	Pipette 5.0 ml barium carrier solution into a 40-ml centrifuge tube, and dilute to 20 ml with distilled water. Add 5 ml ammonium acetate buffer and heat to near boiling in a water bath. Add 1 ml 3N Na_2CrO_4 dropwise and with stirring. Cool, centrifuge, and decant and discard the supernate. Add 5 ml 12N HCl to the barium chromate precipitate. Heat in a water bath until yellow $BaCrO_4$ precipitate dissolves and a white, granular $BaCl_2 \cdot 2H_2O$ precipitate ramains. Cool solution in an ice bath. Add 20 ml cold HCl-diethyl ether reagent. Stir, centrifuge, and decant the supernate. Using several 10-ml portions of cold absolute ethyl alcohol, transfer the precipitate into a tared, scintered-glass filter or Millipore Type OH filter. Wash with three 10-ml portions 95% ethyl alcohol and three 10-ml portions diethyl ether. Place in a desiccator to obtain constant weight. Calculate the weight of barium carrier as $BaCl_2 \cdot 2H_2O$.

Bismuth as bismuth oxide Bi_2O_3 FW 465.958

15 mg Bi^{+3} per ml	Dissolve 16.7 g Bi_2O_3 in 2N HCl and dilute to 1000 ml with 2N HCl.

Calcium as calcium carbonate $CaCO_3$ FW 100.089

20 mg Ca^{+2} per ml

Weigh 49.9 g $CaCO_3$ into a 600-ml beaker. Slowly add 200 ml distilled water and 200 ml 6N HCl until dissolution is complete. Boil to remove CO_2. Cool, and dilute to 1000 ml with distilled water.

Calcium as calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$ FW 236.152

40 mg Ca^{+2} per ml

Dissolve 235.7 g $Ca(NO_3)_2 \cdot 4H_2O$ in 900 ml distilled water. Add 1 ml 16N HNO_3, and dilute to 1000 ml with distilled water.

Cerium as cerous nitrate

(see Scavenger solution)

Iron carrier (scavenger) as ferric chloride $FeCl_3 \cdot 6H_2O$ FW 270.298

5 mg Fe^{+3} per ml

Dissolve 24.2 g of $FeCl_3 \cdot 6H_2O$ in 900 ml distilled water. Add 1 ml 16N HNO_3 and dilute to 1000 ml with distilled water.

(also, see Scavenger solution)

Lanthanum as lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ FW 433.018

20 mg La^{+3} per ml

This reagent should be purified and the purity checked by evaporating 1 ml of reagent on a stainless steel planchet and counting its alpha activity. Less than 0.6 dpm indicates acceptable purity.

a) Dissolve 6.2 g $La(NO_3)_3 \cdot 6H_2O$ in 50 ml distilled water in a 100-ml centrifuge tube.

b) Add a liberal excess of NH_4OH, and centrifuge at 2000 rpm for 10 minutes. Discard supernate.

c) Add 75 ml 6N NH_4OH to precipitate, and mix. Centrifuge at 2000 rpm for 5 minutes, and discard supernate.

d) Repeat c).

e) Add 75 ml distilled water, and mix. Centrifuge as in c), and discard supernate.

f) Dissolve precipitate in a minimum volume of concentrated HNO_3. Dilute to 50 ml with distilled water. Repeat b) through e).

g) Transfer residue to beaker. Add washings, and evaporate to dryness. Cool, and dissolve residue in 100 ml distilled water.

h) Transfer solution to a 125-ml separatory funnel. Add 20 ml TTA solution, shake for 10 minutes, and allow phases to separate.

i) Drain aqueous layer through Whatman No. 542 filter paper into a glass-stoppered reagent bottle. Check the purity. This preparation yields a solution containing approximately 20 mg La^{+3}/ml.

Lead as lead nitrate $Pb(NO_3)_2$ FW 331.200

100 mg Pb^{+2} per ml	Dissolve 159.9 g $Pb(NO_3)_2$ in distilled water and dilute to 1000 ml.
20 mg Pb^{+2} per ml	Dissolve 32.0 g $Pb(NO_3)_2$ in distilled water and dilute to 1000 ml.

Mixed carrier $Sr(NO_3)_2$ FW 211.630; $Zn(NO_3)_2 \cdot 6H_2O$ FW 297.473; $FeCl_3 \cdot 6H_2O$ FW 270.298; $Ni(NO_3)_2 \cdot 6H_2O$ FW 290.813; $Co(NO_3)_2 \cdot 6H_2O$ FW 291.036

22 mg Sr^{+2} per ml 5 mg Zn^{+2} per ml 5 mg Fe^{+3} per ml 5 mg Ni^{+2} per ml 5 mg Co^{+2} per ml	Dissolve 53.2 mg $Sr(NO_3)_2$, 22.8 g $Zn(NO_3)_2 \cdot 6H_2O$, 24.2 g $FeCl_3 \cdot 6H_2O$, 24.8 g $Ni(NO_3)_2 \cdot 6H_2O$, and 24.6 g $Co(NO_3)_2 \cdot 6H_2O$ in 900 ml distilled water. Add 1 ml 16N HNO_3 and dilute to 1000 ml.

Scavenger solution $FeCl_3 \cdot 6H_2O$ FW 270.298; $Ce(NO_3)_3 \cdot 6H_2O$ FW 434.228; $ZrOCl_2 \cdot 8H_2O$ FW 322.249 or $Zr(NO_3)_4 \cdot 5H_2O$ FW 429.318
(mixed iron and rare earth carrier)

20 mg Fe^{+3} per ml 10 mg Ce^{+3} per ml 10 mg Zr^{+4} per ml	Dissolve 96.8 g $FeCl_3 \cdot 6H_2O$, 31.0 g $Ce(NO_3)_3 \cdot 6H_2O$, and 35.3 g $ZrOCl_2 \cdot 8H_2O$ in 900 ml distilled water. Add 1 ml 16N HNO_3, and dilute to 1000 ml with distilled water.
10 mg Fe^{+3} per ml 10 mg Ce^{+3} per ml 10 mg Zr^{+4} per ml	Dissolve 24.2 g $FeCl_3 \cdot 6H_2O$, 15.5 g $Ce(NO_3)_3 \cdot 6H_2O$, and 23.5 g $Zr(NO_3)_4 \cdot 5H_2O$ in distilled water, and dilute to 500 ml.

Strontium as strontium nitrate $Sr(NO_3)_2$ FW 211.630

90 mg Sr^{+2} per ml	Dissolve 217.4 g $Sr(NO_3)_2$ in distilled water. Add 1 ml $16\underline{N}$ HNO_3, and dilute to 1000 ml with distilled water.
88 mg Sr^{+2} per ml	Dissolve 212.6 g $Sr(NO_3)_2$ in distilled water. Add 1 ml $16\underline{N}$ HNO_3, and dilute to 1000 ml with distilled water.
20 mg Sr^{+2} per ml	Dissolve 48.3 g $Sr(NO_3)_2$ in 900 ml distilled water. Add 1 ml $16\underline{N}$ HNO_3, and dilute to 1000 ml with distilled water.
16 mg Sr^{+2} per ml	Dissolve 38.6 g $Sr(NO_3)_2$ in 900 ml distilled water. Add 1 ml $16\underline{N}$ HNO_3, and dilute to 1000 ml with distilled water
8 mg Sr^{+2} per ml	Dissolve 19.3 g $Sr(NO_3)_2$ in 900 ml distilled water. Add 1 ml $16\underline{N}$ HNO_3, and dilute to 1000 ml with distilled water.
Standardization	Pipette 5 ml of carrier solution into a 40-ml centrifuge tube, and dilute to 20 ml with distilled water. Make alkaline with concentrated NH_4OH, and heat to near boiling in a water bath. Add 10 ml $1\underline{N}$ ammonium oxalate, and cool in an ice bath. Filter the solution through a tared, scintered glass filter or Millipore Type OH filter. Wash the precipitate with three 10-ml portions distilled water, three 10-ml portions 95% ethyl alcohol, and three 10-ml portions diethyl ether. Place in a desiccator until constant weight is achieved. Weigh as $SrC_2O_4 \cdot H_2O$.

Yttrium as yttrium nitrate $Y(NO_3)_3$

Note: Yttrium oxide [Y_2O_3 FW 225.81] is used in the preparation of yttrium nitrate carrier because yttrium nitrate from all sources tested contained radioactive contaminants.

20 mg Y^{+3} per ml	Heat (avoid boiling) 25.4 g Y_2O_3 in a minimum volume of $16\underline{N}$ HNO_3 until dissolved. Dilute to 1000 ml with distilled water.
10 mg Y^{+3} per ml	Heat (avoid boiling) 12.7 g Y_2O_3 in 50 ml $16\underline{N}$ HNO_3 until dissolved. Dilute to 900 ml with distilled water. Adjust to pH 2 with concentrated NH_4OH, and dilute to 1000 ml with distilled water.

5 mg Y^{+3} per ml	Heat (avoid boiling) 6.35 g Y_2O_3 in a minimum volume of 16N HNO_3 until dissolved. Dilute to 1000 ml with distilled water
Standardization	Pipette 5 ml carrier solution into a 40-ml centrifuge tube, and dilute to 20 ml with distilled water. Add 10 ml 2N oxalic acid, and adjust the pH to 1.5 with concentrated NH_4OH. Heat to near boiling in a water bath; then cool in an ice bath for 20 minutes. Filter the solution through a tared, scintered-glass filter or Millipore Type OH filter. Wash the precipitate with three 10-ml portions distilled water, three 10-ml portions 95% ethyl alcohol, and three 10-ml portions diethyl ether. Place in a desiccator until constant weight is achieved. Weigh as $Y_2(C_2O_4)_3 \cdot 9H_2O$.

Zirconyl chloride, basic $ZrOCl_2 \cdot 8H_2O$

(see Scavenger solution)

Zirconyl nitrate $Zr(NO_3)_4 \cdot 5H_2O$

(see Scavenger solution)

B.3 TRACER SOLUTIONS

Barium 133 tracer

∿0.02 μCi ^{133}Ba per ml	Dilute 1 ml of 2 μCi/ml barium 133 solution, prepared from a commercially obtained solution, to 100 ml with distilled water.

Strontium 85 tracer

∿3 × 10^4 cpm ^{85}Sr per ml	Transfer an appropriate volume of commercially obtained strontium 85 activity to a 25-ml volumetric flask. Add 1 ml 8N HNO_3, and dilute to volume with distilled water.

B.4 OTHER REAGENTS

Acetic acid CH_3COOH FW 60.053

glacial (17N)	sp gr 1.06, 17.4N, 99.5%
6N	Add 345 ml glacial acetic acid to 800 ml distilled water and dilute to 1000 ml.
1.5N	Add 86.2 ml glacial acetic acid to 800 ml distilled water and dilute to 1000 ml.

Acetone $(CH_3)_2CO$ FW 58.080

Acetone — diethyl ether reagent $(CH_3)_2CO - (C_2H_5)_2O$

1:1 v/v solution	Mix 1 volume of acetone with 1 volume of anhydrous diethyl ether.

Aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ FW 375.136

Crystals	
∿0.45N acidity	Dissolve 745 g $Al(NO_3)_3 \cdot 9H_2O$ in 800 ml distilled water to which 24 ml 16N HNO_3 has been added. Dilute to 1000 ml with distilled water. Standardize.
Standardization	a) Pipette 5 ml reagent into each of three Erlenmeyer flasks. Add 100 ml distilled water and 1 ml methyl orange indicator to each flask. b) Titrate with 0.5N sodium hydroxide to a salmon pink endpoint (pH 3.1). c) Calculate the amount of concentrated HNO_3 (15.55N) necessary to adjust the mineral acidity to 0.45N by the following equation:

$$V_2 = V_1\frac{(0.45 - N_1)}{15.55}$$

where V_1 = aliquot volume of reagent (ml)

V_2 = volume of acid to be added (ml)

N_1 = initial normality of aluminum nitrate, based on b)

d) Add the calculated volume of 15.55N HNO_3 to 5 ml aluminum nitrate reagent, and titrate to check acidity of pH 3.1. This amount of acid is added for each 5 ml of aluminum nitrate reagent prepared.

Ammonium acetate $NH_4C_2H_3O_2$ FW 77.084

6N	Dissolve 462 g $NH_4C_2H_3O_2$ in distilled water and dilute to 1000 ml.
3N	Dissolve 231 g $NH_4C_2H_3O_2$ in 600 ml distilled water and dilute to 1000 ml.

Ammonium acetate buffer

pH 5.0	Dissolve 153 g $NH_4C_2H_3O_2$ in 900 ml of distilled water. Add 28.6 ml glacial acetic acid to adjust the pH to 5, and dilute to 1000 ml with distilled water. Check for pH of 5.0 with a pH meter. Adjust the pH again, if necessary.
pH 4.6	Dissolve 138.5 g of $NH_4C_2H_3O_2$ in 900 ml of distilled water. Add 28.6 ml glacial acetic acid, and dilute to 1000 ml with distilled water. Adjust the pH to 4.6 using a pH meter.

Ammonium carbonate $(NH_4)_2CO_3$ FW 96.087

saturated solution	Dissolve 110 g $(NH_4)_2CO_3$ in 100 ml distilled water. An excess of $(NH_4)_2CO_3$ should be visible.
1/20th saturated	Dilute 5 ml saturated solution to 100 ml with distilled water.

5% w/v	Dissolve 5 g solid $(NH_4)_2CO_3$ in distilled water and dilute to 100 ml.
1% w/v	Dissolve 1 g solid $(NH_4)_2CO_3$ in distilled water and dilute to 100 ml.

Ammonium dichromate $(NH_4)_2Cr_2O_7$ FW 252.066

0.5N (pH 6.5)	Dissolve 252 g $(NH_4)_2Cr_2O_7$ in distilled water. Adjust the pH to 6.5 with NH_4OH or HNO_3, and dilute to 1000 ml with distilled water.
0.05N (pH 6.5)	Dissolve 25.2 g $(NH_4)_2Cr_2O_7$ in distilled water. Adjust the pH to 6.5 with NH_4OH or HNO_3, and dilute to 1000 ml with distilled water.

Ammonium hydroxide NH_4OH FW 35.046

concentrated (15N)	sp gr 0.89-0.90, 14.8N, 58-59%
6N	Dilute 400 ml concentrated NH_4OH to 1000 ml with distilled water.
1N	Dilute 67 ml concentrated NH_4OH to 1000 ml with distilled water.
0.5N	Dilute 33 ml concentrated NH_4OH to 1000 ml with distilled water.

Ammonium molybdate $(NH_4)_2MoO_4$ FW 196.015

0.16M	Dissolve 28.2 g $(NH_4)_2MoO_4$ in distilled water and dilute to 1000 ml.

Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$ FW 142.113

3N	Dissolve 213 g $(NH_4)_2C_2O_4 \cdot H_2O$ in hot distilled water. Cool and dilute to 1000 ml.
1N	Dissolve 71 g $(NH_4)_2C_2O_4 \cdot H_2O$ in hot distilled water. Cool and dilute to 1000 ml.
5% w/v	Dissolve 50 g $(NH_4)_2C_2O_4 \cdot H_2O$ in hot distilled water. Cool and dilute to 1000 ml.

3% w/v	Dissolve 30 g $(NH_4)_2C_2O_4 \cdot H_2O$ in hot distilled water. Cool and dilute to 1000 ml.
0.5% w/v	Dissolve 0.5 g $(NH_4)_2C_2O_4 \cdot H_2O$ in 90 ml distilled water, and dilute to 100 ml.
0.032N	Dissolve 2.27 g $(NH_4)_2C_2O_4 \cdot H_2O$ in 900 ml distilled water and dilute to 1000 ml.
0.03N	Dissolve 2.1 g $(NH_4)_2C_2O_4 \cdot H_2O$ in 900 ml distilled water and dilute to 1000 ml.

Ammonium sulfate $(NH_4)_2SO_4$ FW 132.140

50% w/v	Dissolve 500 g $(NH_4)_2SO_4$ in distilled water and dilute to 1000 ml.

Ammonium vanadate, meta NH_4VO_3 FW 116.979

0.02N	Dissolve 1.17 g NH_4VO_3 in a mixture of 17 ml concentrated perchloric acid and 400 ml distilled water, and dilute to 500 ml with distilled water.

Anion-exchange resin

Dowex 1-X8 (Cl^- form, 50-100 mesh)	Wash the resin with 400 ml of 2N HCl at a flow rate of 2 ml/minute. Continue to wash, using distilled water, until a negative $AgNO_3$ test for Cl^- is obtained on the effluent.
Dowex 1-X4 (Cl^- form, 50-100 mesh)	Wash the resin with 500 ml 6N HCl at a flow rate of 2 ml/minute.

Anstac AC

(see Conducting fluid)

Ascarite 20-30 mesh

Ascorbic acid $C_6H_8O_6$ FW 176.126

white crystalline powder

Bromcresol green $C_6H_4SO_2OC(C_6H\text{-}3,5\text{-}Br_2\text{-}2\text{-}CH_3\text{-}4\text{-}OH)_2$ FW 698.040

0.1% w/v in ethyl alcohol

Dissolve 0.1 g bromcresol green in 100 ml 20% ethyl alcohol.

Cal-Red indicator, dilute

1% w/v

Obtained from Scientific Service Laboratories, Inc., P. O. Box 175, Dallas, Texas 75221

Carbon tetrachloride CCl_4 FW 153.823

Cation-exchange resin

Dowex 50W-X8 (H^+ form, 50-100 mesh)

Wash 10 ml of the resin with 100 ml distilled water at a flow rate of 10 ml/minute to remove excess acid.

Dowex 50W-X8 (Na^+ form, 50-100 mesh)

Wash 170 ml of the resin with 1500 ml 4N NaCl at a flow rate of 10 ml/minute. Then wash with 500 ml of distilled water. Test effluent with $AgNO_3$ to be sure all excess Cl^- has been removed from the resin.

Citrate solution

3N (pH 6.5)

Dissolve 210.1 g $H_3C_6H_5O_7 \cdot H_2O$ in 500 ml distilled water. Using a pH meter, adjust pH of solution to 6.5 with 12N NaOH (approximately 220 ml). Dilute to 1000 ml with distilled water.

Citric acid $H_3C_6H_5O_7 \cdot H_2O$ FW 210.141

granular

Conducting fluid

Anstac AC

Obtained from Chemical Development Corporation, Danvers, Massachusetts. Prepare according to manufacturer's directions.

Detergent

Diethyl ether $(C_2H_5)_2O$ FW 74.123

anhydrous	BP 34.6° C

Di(2-ethyl-hexyl)phosphoric acid [HDEHP]

20% v/v in toluene	Mix 20 ml HDEHP with 80 ml toluene.
5% v/v in toluene	Mix 5 ml HDEHP with 95 ml toluene.

Disodium ethylenediamine tetraacetate [EDTA] $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$ FW 372.242

0.04N	Dissolve 7.44 g EDTA in 900 ml of distilled water and dilute to 1000 ml.
10% w/v	Dissolve 100 g EDTA in 900 ml of distilled water and dilute to 1000 ml.
0.02 N	Dissolve 3.72 g EDTA in 900 ml of distilled water and dilute to 1000 ml.

EDTA

(see Disodium ethylenediamine tetraacetate)

Ethyl acetate $CH_3COOC_2H_5$ FW 88.107

Ethyl alcohol C_2H_5OH

absolute (100%)	99.5% pure, 0.5% benzene
95%	USP
20% v/v	Dilute 20 ml 95% ethyl alcohol to 95 ml with distilled water.

Ethyl ether

(see Diethyl ether)

Ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ FW 404.001

0.27N	Dissolve 36.4 g $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water and dilute to 1000 ml.

Formaldehyde HCHO FW 30.026

37%	36-38% by weight, commercial solution

HDEHP

(see Di(2-ethyl-hexyl)phosphoric acid)

Hydrochloric acid HCl FW 36.461

concentrated (12N)	sp gr 1.185-1.192, 12.1N, 37%
9N	Add 750 ml concentrated HCl to distilled water, and dilute to 1000 ml.
8N	Add 666 ml concentrated HCl to distilled water, and dilute to 1000 ml.
6N	Add 500 ml concentrated HCl to distilled water, and dilute to 1000 ml.
4N	Add 333 ml concentrated HCl to distilled water, and dilute to 1000 ml.
3.5N	Add 300 ml concentrated HCl to distilled water, and dilute to 1000 ml.
3N	Add 250 ml concentrated HCl to distilled water, and dilute to 1000 ml.
2N	Add 167 ml concentrated HCl to distilled water, and dilute to 1000 ml.
1.8N	Add 150 ml concentrated HCl to distilled water, and dilute to 1000 ml.
1N	Add 83 ml concentrated HCl to distilled water, and dilute to 1000 ml.
5% v/v in alcohol	Add 5 ml concentrated HCl to absolute ethyl alcohol and dilute to 100 ml.
0.5N	Add 41.7 ml concentrated HCl to distilled water, and dulute to 1000 ml.
0.1N	Add 8.3 ml concentrated HCl to distilled water, and dilute to 1000 ml.
0.06N adjusted to pH 1.4	Add 5 ml concentrated HCl to 1000 ml distilled water and adjust pH to 1.4 using a pH meter.

0.05N	Dilute 500 ml 0.1N HCl to 1000 ml with distilled water.

Hydrochloric acid — absolute alcohol

5:100 v/v solution	Mix 5 ml 12N HCl with 100 ml absolute ethyl alcohol.

Hydrochloric acid — diethyl ether $HCl\text{-}(C_2H_5)_2O$

5:1 v/v solution	Mix 5 volumes of concentrated HCl with 1 volume of anhydrous diethyl ether. Add ether to HCl.
1:1 v/v solution	Mix 1 volume of 12N HCl with 1 volume of anhydrous diethyl ether. Add ether to HCl.

Hydrofluoric acid HF FW 20.006

concentrated (48%)	sp gr 1.15, 48%
1.5N	Add 22 ml concentrated HF to distilled water and dilute to 400 ml.

Hydrogen peroxide H_2O_2 FW 34.015

30% solution	30-32% commercial solution

Hydrogen sulfide H_2S

gas

8-Hydroxyquinoline

(see Quinolinol)

Hydroxylamine hydrochloride $NH_2OH \cdot HCl$ FW 69.491

crystals	
5% w/v in ethyl alcohol	Dissolve 5 g $NH_2OH \cdot HCl$ in 95 ml 95% ethyl alcohol and dilute to 100 ml with alcohol

Lucite

0.5 mg/ml in acetone	Dissolve 50 mg lucite in 100 ml acetone.

Magnesium perchlorate $Mg(ClO_4)_2$ FW 223.213

anhydrous	(10-20 mesh)

Methyl orange indicator $4\text{-}NaOSO_2C_6H_4N{:}NC_6H_4\text{-}4\text{-}N(CH_3)_2$ FW 327.339

0.1% w/v	Dissolve 0.1 g methyl orange in distilled water and dilute to 100 ml. Filter if necessary.
0.05% w/v	Dissolve 0.05 g methyl orange in distilled water and dilute to 100 ml. Filter if necessary.

Methyl red indicator $4\text{-}(CH_3)_2NC_6H_4N{:}NC_6H_4\text{-}2\text{-}COOH$ FW 269.305

0.1% w/v	Dissolve 0.1 g methyl red in distilled water and dilute to 100 ml. Filter if necessary.

Nickel sulfate $NiSO_4 \cdot 6H_2O$ FW 262.864

crystals	
0.5M plating solution	Dissolve 13.1 g $NiSO_4 \cdot 6H_2O$ in 100 ml of concentrated HN_4OH.

Nitric acid HNO_3 FW 63.016

fuming (90%)	sp gr 1.50, 90%
75% w/v	Cautiously dilute 333 ml fuming HNO_3 to 1000 ml with 16N HNO_3.
concentrated (16N)	sp gr 1.416-1.426, 15.5N, 70%
14N	Dilute 875 ml 16N HNO_3 to 1000 ml with distilled water. Add acid to water.
9N	Dilute 562 ml 16N HNO_3 to 1000 ml with distilled water. Add acid to water.

8N	Dilute 500 ml 16N HNO_3 to 1000 ml with distilled water. Add acid to water.
6N	Add 375 ml 16N HNO_3 to distilled water and dilute to 1000 ml.
4N	Add 250 ml 16N HNO_3 to distilled water and dilute to 1000 ml.
3N	Add 187 ml 16N HNO_3 to distilled water and dilute to 1000 ml.
7.5% v/v	Add 75 ml 16N HNO_3 to distilled water and dilute to 1000 ml.
1N	Add 62.5 ml 16N HNO_3 to distilled water and dilute to 1000 ml.
0.5N	Add 31.25 ml 16N HNO_3 to distilled water and dilute to 1000 ml.
0.1N	Add 6.25 ml 16N HNO_3 to distilled water and dilute to 1000 ml.

Oxalic acid $H_2C_2O_4 \cdot 2H_2O$ FW 126.066

saturated at room temperature	Approximately a 2N solution.
2N	Dissolve 126 g $H_2C_2O_4 \cdot 2H_2O$ in 900 ml warm distilled water. Let cool to room temperature and dilute to 1000 ml.
1N	Dissolve 63.0 g $H_2C_2O_4 \cdot 2H_2O$ in 900 ml distilled water and dilute to 1000 ml.
2.5% w/v	Dissolve 25.0 g $H_2C_2O_4 \cdot 2H_2O$ in 900 ml distilled water and dilute to 1000 ml.

Perchloric acid $HClO_4$ FW 100.459

concentrated (12N)	sp gr 1.67, 11.6N, 70-72%

Phenolphthalein indicator $C_{20}H_{14}O_4$ FW 318.330

1% w/v in alcohol	Dissolve 1.0 g phenolphthalein in 80 ml of 95% ethyl alcohol, and dilute to 100 ml.
0.1% w/v in alcohol	Dissolve 0.1 g phenolphthalein in 80 ml of 95% ethyl alcohol, and dilute to 100 ml.

o-Phosphoric acid H_3PO_4 FW 97.996

concentrated (44.0N)	85%

Potassium blank solution

(see B.1 STANDARD SOLUTIONS)

Potassium dichromate $K_2Cr_2O_7$ FW 294.192

1N	Dissolve 147 g $K_2Cr_2O_7$ in distilled water and dilute to 1000 ml.

Potassium hydroxide KOH FW 56.109

8N	Dissolve 449 g KOH in distilled water and dilute to 1000 ml.
5N	Dissolve 280 g KOH in distilled water and dilute to 1000 ml.
2N	Dissolve 112 g KOH in distilled water and dilute to 1000 ml.

Potassium permanganate

(see B.1 STANDARD SOLUTIONS)

Quinolinol [8-hydroxyquinoline] $HO\underbrace{C_6H_3N{:}CHCH{:}CH}$ FW 145.163

7.5% w/v in methanol	Dissolve 7.5 g quinolinol in methanol and dilute to 100 ml.

Scavenger solution

(see B.2 CARRIER SOLUTIONS)

Scintillation medium

dioxane solvent	Dissolve 4.0 g 2,5-diphenyl-oxazole [PPO], 0.05 g 1,4-bis-2 (5-phenyl-oxozolyl)-benzene [POPOP], and 120 g naphthalene in 1000 ml of *p*-dioxane. All reagents should be spectro-quality or scintillation grade. The *p*-dioxane must be freshly opened. If not, distillation is

necessary. The mixture is stable for approximately 2 weeks.

Sodium acetate $NaC_2H_3O_2$ FW 82.035

20% w/v	Dissolve 200 g $NaC_2H_3O_2$ in 900 ml distilled water and dilute to 1000 ml.

Sodium bisulfite $NaHSO_3$ FW 104.060

1N	Dissolve 104 g $NaHSO_3$ in 800 ml distilled water and dilute to 1000 ml.

Sodium carbonate Na_2CO_3 FW 105.989

anhydrous granules or powder

3N	Dissolve 159 g Na_2CO_3 in 900 ml distilled water and dilute to 1000 ml.
2N	Dissolve 106 g Na_2CO_3 in 900 ml distilled water and dilute to 1000 ml.
0.1N	Dissolve 5.30 g Na_2CO_3 in 900 ml distilled water and dilute to 1000 ml.

Sodium chloride NaCl FW 58.443

crystals

4N	Dissolve 234 g NaCl in 900 ml distilled water and dilute to 1000 ml.
5% w/v	Dissolve 5 g NaCl in 900 ml distilled water and dilute to 100 ml.

Sodium chromate Na_2CrO_4 FW 161.973

6N	Dissolve 486 g Na_2CrO_4 in 900 ml distilled water and dilute to 1000 ml.
3N	Dissolve 243 g Na_2CrO_4 in 900 ml distilled water and dilute to 1000 ml.
1N	Dissolve 81 g Na_2CrO_4 in 900 ml distilled water and dilute to 1000 ml.
0.6N	Dissolve 48.6 g Na_2CrO_4 in 900 ml distilled water and dilute to 1000 ml.

0.25N	Dissolve 20.25 g Na_2CrO_4 in 900 ml distilled water and dilute to 1000 ml.

Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$ FW 297.998

cleaning solution	Dissolve 35 ml saturated solution of $Na_2Cr_2O_7 \cdot 2H_2O$ in 900 ml concentrated sulfuric acid and dilute to 1000 ml with concentrated sulfuric acid.
3N	Dissolve 447 g $Na_2Cr_2O_7 \cdot 2H_2O$ in distilled water and dilute to 1000 ml.
0.5N	Dissolve 74.5 g $Na_2Cr_2O_7 \cdot 2H_2O$ in distilled water and dilute to 1000 ml.

Sodium hydroxide NaOH FW 39.998

pellets	USP
12N	Dissolve 480 g NaOH in 900 ml distilled water and dilute to 1000 ml.
10N	Dissolve 400 g NaOH in 900 ml distilled water and dilute to 1000 ml.
6N	Dissolve 240 g NaOH in 900 ml distilled water and dilute to 1000 ml.
1N	Dissolve 40 g NaOH in 900 ml distilled water and dilute to 1000 ml.

Sodium hypochlorite NaOCl FW 74.442

5% solution	Commercial grade, 4-6% NaOCl

Sodium nitrite $NaNO_2$ FW 68.996

2N	Dissolve 1.38 g $NaNO_2$ in distilled water and dilute to 10 ml.
1N	Dissolve 69.0 g $NaNO_2$ in 800 ml distilled water and dilute to 1000 ml.

Sodium oxalate

(see B.1 STANDARD SOLUTIONS)

Sulfuric acid H_2SO_4 FW 98.078

concentrated (36N)	sp gr 1.8407-1.8437, 36.0N, 95-98%
2N	Dilute 55.6 ml concentrated H_2SO_4 to 1000 ml with distilled water. Carefully add acid to water.
1N	Dilute 27.8 ml concentrated H_2SO_4 to 1000 ml with distilled water. Carefully add acid to water.
0.5N	Dilute 13.9 ml concentrated H_2SO_4 to 1000 ml with distilled water. Carefully add acid to water.

TBP

(see Tri-*n*-butyl phosphate)

TCA

(see Trichloroacetic acid)

2-Thenoyltrifluoroacetone [TTA] 4,4,4-trifluoro-1(2-thienyl)-1,3-butanedione

10% w/v in benzene	Dissolve 100 g TTA in benzene and dilute to 1000 ml.
5.6% w/v in xylene	Dissolve 5.55 g TTA in 100 ml xylene.

Toluene $C_6H_5CH_3$ FW 92.141

for HDEHP reagent	sp gr 0.866, BP 110.6° C

Tri-*n*-butyl phosphate [TBP] $(C_4H_9)_3PO_4$ FW 226.323

pre-equilibrated with 14N HNO_3	Add 150 ml distilled water and 30 ml 3N Na_2CO_3 to 300 ml of TBP in a 1-liter separatory funnel. Equilibrate by shaking for 2-3 minutes. Allow phases to separate, and drain off and discard lower aqueous phase. Add 150 ml distilled water to the separatory funnel, and equilibrate for 2-3 minutes. Allow phases to separate, and discard lower aqueous phase. Add 150 ml 14N HNO_3 to the separatory funnel, and equilibrate for 5 minutes. Allow

phases to separate, and discard lower aqueous phase. Repeat this $14\underline{N}$ HNO_3 treatment twice.

Trichloroacetic acid [TCA] CCl_3COOH FW 163.388

50% w/v	Dissolve 500 g CCl_3COOH in 500 ml distilled water and dilute to 1000 ml.
5% w/v	Dissolve 50 g CCl_3COOH in 900 ml distilled water and dilute to 1000 ml.

TTA

(see 2-Thenoyltrifluoroacetone)

Tygon thinner

commercial grade	Obtained from U. S. Stoneware, Akron, Ohio.

Water H_2O

distilled	Distill, demineralize, or deionize water to contain not more than 5.0 ppm of dissolved solids and to have an electrical conductivity of not more than 8 micromhos per centimeter at 25° C.
reagent	In general, distilled water as described above is adequate for use in procedures of this manual. Strictly speaking, high purity reagent water should meet the more stringent American Chemical Society specifications for distilled water(2).

Xylene $C_6H_4(CH_3)_2$ FW 106.168

B.5 REFERENCES

1. *Handbook of Chemistry and Physics, 45th Edition, 1964-1965.* Cleveland, Chemical Rubber Company (1964) page B-1

2. American Chemical Society, Committee on Analytical Reagents. *Reagent Chemicals, American Chemical Society Specifications, 1960.* Washington, Applied Publications, American Chemical Society (1961)

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